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THE DISTRIBUTION OF INTENSITY IN THE RAMAN SPECTRUM OF DIAMOND

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(Communicated by Prof. R. S. Krishnan, F.A.SC.)

1. Introduction

The theory of the normal vibrations of crystal lattices developed by Sir C. V. Raman (1943) leads to the result that the crystal structure of diamond has eight monochromatic frequencies of vibration. Of these, one is triply degenerate, two are four-fold degenerate, three are six-fold degenerate and two are eight-fold degenerate. From the nature of the modes, it follows that only the triply degenerate mode would be Raman-active in the first approximation, and hence only one frequency shift should be ordinarily observed in the spectrum of light-scattering by diamond, as is actually found to be the case (Ramaswamy, 1930). In the second approximation, however, all the modes should be active in greater or less measure. Accordingly, it is to be expected that when adequate exposures are given, frequency shifts corresponding to overtones and combinations of the eight fundamental frequencies should be observable. Their intensities would be determined by the second-order changes of optical polarisability arising in each case and hence would necessarily be small.

The theoretical prediction stated above was strikingly confirmed by the investigations of R. S. Krishnan commenced in 1944 and continued in later years. Even in his earliest studies made with a tiny diamond only 40 milligrams in weight, a second-order spectrum exhibiting a structure of the kind indicated by the theory was recorded. Subsequently, a plate of diamond became available which weighed 245 milligrams and was fully transparent to the λ 2537 rays of the mercury arc. The use of this larger specimen made it possible to employ more powerful spectrographs and to photograph the second-order spectrum under high resolution and dispersion. The published reproductions of the original spectra thus obtained and their

microphotometric records exhibit the discrete character predicted by the theory in an unmistakeable fashion (R. S. Krishnan, 1947).

The distribution of intensity in the second-order Raman spectrum of diamond is a matter of considerable interest. Remarkably enough, the octaves of some of the inactive modes surpass in intensity the octave of the principal or active Raman frequency, while on the other hand, there are other octaves and combinations which appear with much smaller intensities. It has been shown by Sir C. V. Raman (1947) that these features follow necessarily as a consequence of the particular modes of vibration prescribed by the theory. The quantitative estimation of the relative intensities of the various features observable in the second-order Raman spectrum of diamond thus acquires a measure of importance. It is proposed here to present some studies on this subject made by the author. The data obtained are specially significant in relation to the claims made by Miss Helen Smith, a pupil of Professor Max Born, in a paper on the Raman spectrum of diamond (1948). Indeed, the present investigation demonstrates that the consequences of the Born-Karman lattice dynamics developed in Miss Smith's paper for the case of diamond are toally incompatible with the observed behaviour of that substance in the Raman effect.

2. Some Consequences of the Theory

It will be useful here to give a brief resumé of the features theoretically to be expected in the second-order spectrum of diamond. A rigorous calculation of the eight fundamental frequencies of vibration of the diamond structure has been made by K. G. Ramanathan (1947), taking into account the forces between each atom and its 28 nearest neighbours. Expressed in wave-numbers, they came out as follows, the number enclosed in brackets being the respective degeneracies: 1332 (3), 1250 (8), 1232 (6), 1149 (4), 1088 (6), 1008 (4), 752 (6) and 620 (8). The triply degenerate mode having the highest frequency is Raman-active by reason of its symmetry characters. The other modes are inactive in the first order by reason of the fact that the vibrations are in opposite phases in adjacent cells of the lattice, and the resulting variations of optical polarisability therefore cancel out. In the two modes of lowest frequency, the bonds between adjacent carbon atoms do not vary in length; only the bond-angles alter. Hence, the variations of optical polarisability arising in these two modes are negligibly small and they cannot therefore appear either as overtones or as combinations with other modes. The octaves and summations of the remaining six modes are listed below in wave-numbers, the octaves being shown in heavy type along the diagonal of the square.

TABLE I

Octaves and Summational Frequencies

2664	2582	2564	2481	2420	2340
	2500	2482	2399	2338	2258
		2464	2381	2320	2240
			2298	2237	2157
				2176	2096
					2016

Thus, a maximum of twenty-one frequency-shifts may be expected in the second-order spectrum, the highest and lowest being 2664 and 2016 respectively.

To obtain a more definite picture of the observable facts, we have to consider also the question of intensities. The factors determining them would be, *firstly*, the amplitude of variation of the C–C bond-lengths, and *secondly*, the number of bond-lengths which vary in each unit of the structure. Since we are concerned with second-order variations of optical polarisability, the first of these two factors assumes special importance. It is not the same in the different modes, and as a consequence of this, the mode appearing most strongly in the second-order spectrum would be the octave of the third fundamental and not of the first or the second, though the latter would also have fair intensities. Further, the same considerations indicate that the octave of the fifth fundamental would appear with less intensity than the octaves of the first four fundamentals; also that the octave of the sixth fundamental would be extremely weak.

Some additional features of importance need to be mentioned. The appearance of a mode of vibration as a frequency shift in the second-order spectrum is a consequence of its finite amplitude. Hence, it is necessary to consider the influence of anharmonicity on the frequencies. In particular, since the fundamental frequencies are themselves degenerate, their combination may be expected to result in a removal of the degeneracy, in other words, in a splitting of each combinational frequency into several distinct components. We notice also that in Table I there is a crowding

together of the lines in a particular region of the spectrum. Fourteen of them are concentrated in the region of frequency shifts between 2500 and 2200 wave-numbers, and some of the frequencies are also nearly coincident. In these circumstances, perturbations of frequency are likely to arise by reason of the mutual interactions between the different modes. We have thus reason to anticipate that the shifts of frequency actually observed in the second-order spectrum would not be exactly those listed in the table, and that both displacements and additional components are possible.

3. The Experimental Facts

It will be evident from what has been stated above that the second-order Raman spectrum of diamond would be a closely spaced aggregate of lines. The test for ascertaining whether it is actually of that nature is to use a spectrograph of high resolving power; such an instrument would reveal the fine structure of the spectrum clearly even if an instrument of lower power fails to do so. On the other hand, a spectrum which is continuous or consists of diffuse bands would exhibit the same aspect with both the high and low resolving powers.

Three different instruments, *viz.*, the "intermediate", "medium" and "large" quartz spectrographs of Hilger were used by R. S. Krishnan in his investigations, and the spectrograms published by him show notable increases in the clarity of the spectrum and more detail visible in it with the higher resolving power. The spectrum recorded by the "large" quartz spectrograph is reproduced in the issue of *Nature*, dated the 11th of January 1947, and very clearly exhibits twelve sharply defined lines; the power of the instrument as well as the nature of the spectrum itself are both revealed by the fact that the two lines of greatest intensity having wave-number shifts of 2460 and 2470 respectively are seen clearly resolved from each other. Indeed, they are as sharply defined as the lines of the mercury arc or the line with frequency shift 2664 which is the octave of the principal Raman frequency. The detailed paper by R. S. Krishnan published in the *Proceedings of the Academy* for December 1947 contains reproductions of the spectra recorded with the "medium" as well as the "large" instrument. A series of microphotometer traces of these spectra are also reproduced with that paper and they show all the features visually observed in the spectra. For instance, the doublet with frequency shifts 2460 and 2470 is seen to be such both in the spectrum and in the microphotometer record, obtained with the more powerful instrument.

The frequency shifts actually observed are entered in Table II in the same manner as in Table I to facilitate comparison with the latter. The

TABLE II

Observed Frequency Shifts

2665 (4)	*2595* *2565*	*2547* 2536 (3)	2490 (4) 2470 (3)	2440 (4)	2334 (4)
	2520 (4) 2502 (4)	**2490** (4) **2470** (3)		2334 (4)	2255 (5)
		2470 (3) **2460** (3)		2334 (4)	2255 (5)
			2297 (4)	2255 (5) 2225 (3)	
				2190 **2176** (4)	
					2015

lines which are most conspicuous in the spectrograms are shown in heavy type, the less conspicuous ones in ordinary type and the least conspicuous in italics. The small figures shown in brackets after the wave-number shifts are the respective line-widths estimated from the spectra and their microphotometer traces. It will be noticed that some of the frequency shifts appear more than once, indicating that alternative assignments are possible. It will also be noticed that in some cases, there is a splitting of the frequencies. There are only four blank cages in Table II as compared with Table I. The gaps in the fourth vertical column are due to the presence of mercury lines which make frequency shifts near 2400 unobservable. The gaps in the last vertical column represent combinations which are unobservable by reason of the very low intensity to be expected in those cases.

4. MICROPHOTOMETRIC STUDY OF THE SPECTRUM

The material set out briefly in the two preceding sections makes it evident that the observed behaviour of diamond in the Raman effect is in full accord with that to be expected on the basis of the new crystal dynamics. What the experimental facts prove is that the fundamental vibration frequencies—the overtones and combinations of which appear as frequency

shifts—form a line spectrum and *not* a diffuse or continuous one as contemplated in the older theories. This conclusion is of such fundamental and far-reaching importance that it is not superfluous to put forward further experimental evidence in support of it. Such confirmatory evidence is forthcoming on an examination of the microphotometer traces of the spectrum recorded under appropriate conditions.

To ascertain the distribution of intensity in the Raman spectrum, it is necessary to avoid or eliminate the background of false illumination recorded simultaneously with it on the photographic plate. This is a matter of great importance in view of the extreme faintness of the second-order spectrum. The radiations diffused or scattered by the diamond and entering the spectrograph have to traverse its optical system before they reach the photographic plate. Since even the most perfect optical surfaces scatter light to some extent, a diffuse continuum appears overlying the real spectrum. The screen of mercury vapour employed in the experiments eliminates the part of this continuum due to the intense λ 2537 radiations of the mercury arc. But the rest of the radiations entering the spectrograph are not thus eliminated and give rise to disturbing effects. The background illumination arising from their presence is found to be relatively more intense with the "large" quartz spectrograph which is of the Littrow type than with the "medium" instrument in which the light traverses the optical train only once. The superior resolution and dispersion provided by the former instrument are useful when it is sought to exhibit the maximum of detail in the spectrum. But the freedom from background of the "medium" spectrograph makes it the appropriate instrument to employ for an investigation of distribution of intensity in the Raman spectrum; it offers also the additional advantage of a vastly greater speed. It has accordingly been used in the present studies which have been made with the same diamond as in R. S. Krishnan's previous work; this is a thick semi-circular plate which is held so that the light from the mercury arc enters the flat face and the scattered light emerges through the edge and enters the spectrograph. The edge which was originally somewhat irregular was smoothed and polished for the purpose of the present investigation. A notable improvement in the recorded spectra has resulted therefrom.

The character of the second-order spectrum and the distribution of intensity in it are elucidated by the following procedure. The spectrum is photographed with a graduated series of exposures, commencing with one of just sufficient duration to record the most intense regions in it, and ending with an exposure sufficiently prolonged for the spectrum itself to be heavily

over-exposed, but without a background coming up having any appreciable intensity. The sequence of spectrograms thus obtained is very instructive; the earlier ones show the more intense features very clearly, while the later ones show the fainter parts best. The microphotometer records of the series of spectrograms show a progressive change in character. The *minor* variations of intensity within the spectrum are less conspicuous in the microphotometer records of the heavily exposed spectrograms; on the other hand, the *major* features remain and are indeed much more strikingly evident than in the microphotometer traces of the weakly exposed spectra.

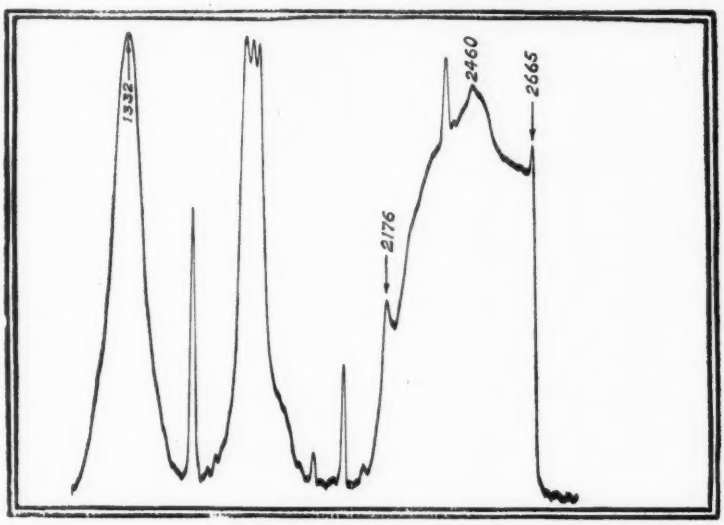

FIG. 1. Microphotometer Record of Heavily Exposed Second-Order Spectrum (Medium Spectrograph)

Fig. 1 reproduces the microphotometer records of a heavily exposed spectrogram. Reading it from right to left, we notice an *abrupt rise in intensity from zero to a sharply defined peak at a frequency shift of 2665 wave-numbers*, followed again by a steep fall. Reading the record from left to right, we notice another *abrupt rise of intensity from zero to a sharply defined peak at a frequency shift of 2176 wave-numbers*, followed again by a rapid fall. Still another narrow peak of maximum intensity appears nearly midway between these at 2460 wave-numbers. Thus, the microphotometer record indicates the presence in the spectrum of three sharply-defined lines whose widths do not exceed a few wave-numbers in each case and having frequency

shifts 2665, 2460 and 2176 respectively. That this is actually the case is visually evident also from the series of spectrograms recorded with moderate exposures and reproduced as Figs. 1 (*a*), (*b*), (*c*) and (*d*) of Plate I.

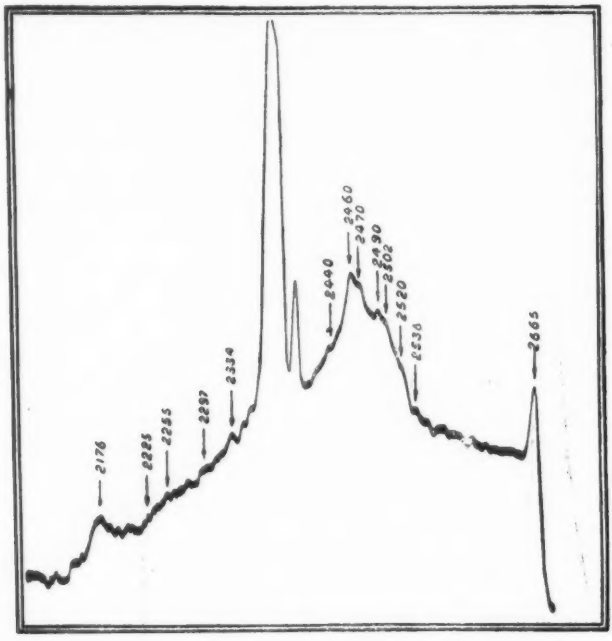

FIG. 2. Microphotometer Record of Moderately Exposed Second-order Spectrum (Large Spectrograph)

The remarks made earlier concerning the relative merits of the " medium " and the " large " spectrographs may be illustrated by a comparison between Figs. 1 and 2 above. Far more detail is visible in the latter than in the former, while only a hint of a fine structure is visible in the former. This is partly because of the heavy exposure employed in the latter case which tends to obliterate the finer details and partly also because of the inadequate power of the smaller instrument. On the other hand, it would scarcely have been possible with the larger instrument to obtain a spectrogram so heavily exposed and so free from background as to exhibit the discontinuous drop of intensity at 2176 wave-numbers seen in Fig. 1. The advantage of the larger instrument thus lies in its capacity to resolve and exhibit the finer details of structure of the spectrum. This will be evident also on a com-

parison of Fig. 1 (*b*) in Plate I with Fig. 2 in Plate II, taken respectively with the smaller and larger instruments. The exposures in the two cases were such as to yield negatives of comparable densities.

5. Distribution of Intensity in the Spectrum

A microphotometer record does not, of course, represent the actual distribution of intensity, but bears a certain relationship to it determined by the contrast-quality of the photographic plate as well as by the exposure and the development. A microphotometer record can, however, be translated into an intensity curve by appropriate methods, and this has been done in the present case. For this purpose, the photographic plates used were calibrated with the help of the continuous radiation from a hydrogen discharge tube, a set of graded intensity marks being recorded on them alongside of the spectrum. The density versus intensity curve for the wave-length λ 2700 was drawn for the plates by running them through the microphotometer. The data thus obtained enabled the intensity distribution in the Raman spectrum of the second order to be evaluated. No attempt has been made to correct for the finite slit-widths (0·025—0·04 mm.) actually employed in photographing the spectra.

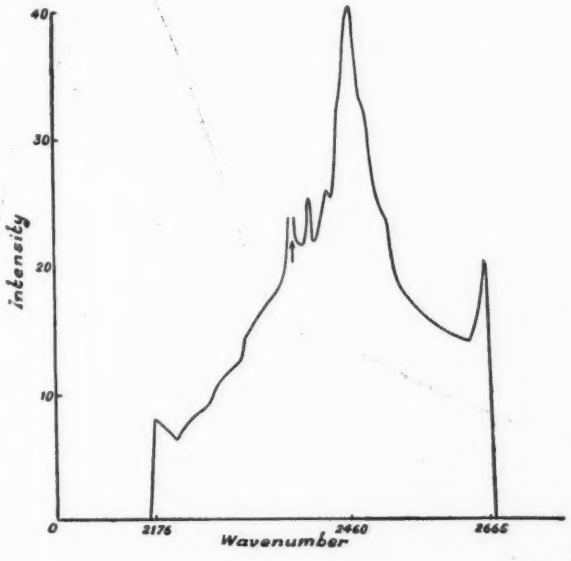

Fig. 3. Intensity Curve of Second-Order Raman Spectrum of Diamond

Fig. 3 above is a sketch of the intensity-curve deduced in the manner explained from the microphotometer records. Since the spectrograms from which it was derived were obtained with an instrument of moderate resolving power, it cannot claim to represent the finer details of the variations of intensity in the spectrum, as for instance those shown in Fig. 2 above, with any degree of fidelity. There can be no doubt, however, as to the correctness of the main features appearing in it. Reading from right to left, we find in the diagram, (1) a steep straight rise of intensity from zero to an extremely sharp peak at 2665 wave-numbers, (2) a trough of low intensity following it and extending up to 2500 wave-numbers, (3) a rapid rise following this and culminating in the great peak of intensity at 2460 wave-numbers, (4) the subsequent rapid fall leading to a trough of low intensity at 2200 wave-numbers, (5) the rise following this to a well-defined peak at 2176 wave-numbers and (6) the subsequent sudden drop to zero. All these features appear also in Fig. 1 above, except that the actual variations of intensity are much more pronounced than the ups and downs of the microphotometer record for the denser regions of the spectrographic negative.

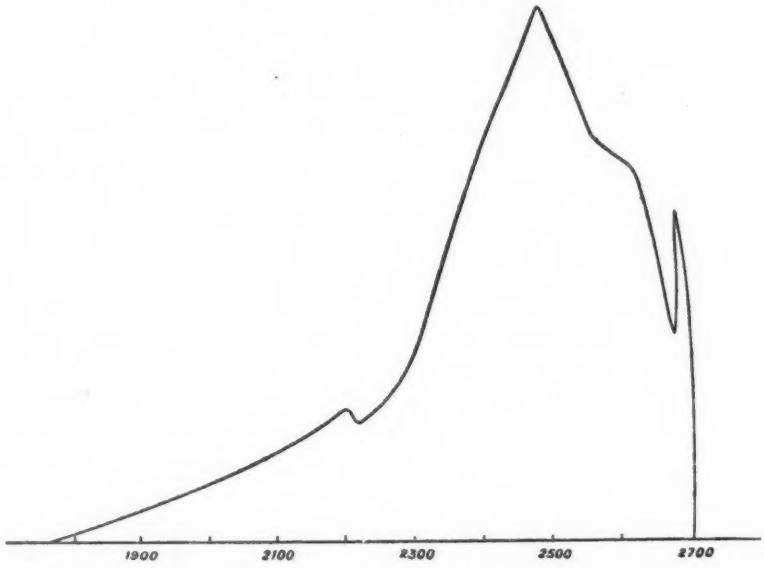

FIG. 4. Intensity Distribution according to the Born-Karman Theory

In the paper by Miss Helen Smith cited above, there appears a curve claiming to represent the distribution of intensity in the Raman spectrum expected theoretically on the basis of the Born-Karman lattice dynamics.

This curve is reproduced above (Fig. 4) on the same scale of wave-numbers as Fig. 3 for comparison with the distribution of intensity derived from observation and shown in the latter. It will be noticed that none of the characteristic features of Fig. 3 listed above appear in Fig. 4, while on the other hand, the latter exhibits several curious features for which there is no counterpart in the experimentally determined intensity distribution.

6. The Born-Karman Theory and Its Consequences

The reasons for the striking lack of resemblance between the actual distribution of intensity in the Raman spectrum of diamond and that put forward in Miss Helen Smith's paper will become clear when we consider the process by which the curve reproduced above in Fig. 4 was constructed by her.

As is well known, the Born-Karman lattice dynamics bases itself on the idea that the possible vibrations of the atoms in a crystal can be described as waves in the solid, their lengths and directions being those defined by the cyclic postulate. An immense number of waves is possible according to the postulate, and the vibration spectrum of the crystal deduced therefrom, becomes a continuum stretching from zero frequency upwards to a high limit. A great part of Miss Helen Smith's paper is taken up with a calculation of the frequency distribution in the vibration spectrum of diamond, and for this purpose of these calculations, the distribution is represented as the sum of six separate distributions or branches. Three of these branches lie in the higher part of the frequency range, one of them extends throughout the whole range and the remaining two others lie in its lower part. From these six frequency distributions again, are derived thirteen others representing the octaves, sums and differences of their respective frequencies. Branches 1, 2, 3 and 6 lie in the upper part of the frequency range, 4, 5, 7, 8 and 9 appear in the middle of the range, while 10, 11, 12 and 13 lie in its lower parts. To derive the intensity distribution in the second-order spectrum, it is *assumed* that the light-scattering power associated with the branches 4, 5, 7, 8, 9, 11, 12 and 13 is zero, while to the branches 1, 2, 3 and 6 are assigned respectively the relative scattering powers 1 : 40 : 12 : 1. The ordinates of these four curves are added up and the curve shown above in Fig. 4 is thus derived.

We may remark in the first place, that no reason or physical justification is given in Miss Smith's paper for the assumption made that most of branches are ineffective, as also for selecting only four of them as operative and assigning to them the specific ratios quoted above. These arbitrary assumptions were evidently made for securing a pre-determined result, *viz.*, a graph which—without any regard being paid to its actual shape or specific features—would exhibit humps at 2665, 2460 and 2176 wave-numbers,

A paper of 1946 by R. S. Krishnan is quoted by Miss Smith in this connection. But one can find as little resemblance between the microphotometer curve appearing in that paper and the " theoretical " diagram of Miss Smith as there is between Fig. 3 and Fig. 4 in the present paper. Indeed, the microphotometer record reproduced in Krishnan's paper of 1946 is of a spectrum taken with moderate exposures and the " medium " spectrograph, and it shows much recognizable detail besides three sharp peaks at the positions mentioned above. It is quite gratuitously suggested in Miss Smith's paper that all such details were spurious features. That such a suggestion should have been put forward is the more surprising in view of the publication by R. S. Krishnan of a note in *Nature* of the 11th January 1947, in which a spectrogram is reproduced showing very clearly the presence of 12 sharply defined lines in the very same regions of the spectrum. It is very strange also that no reference appears in Miss Smith's paper either to this note or to the two later ones in *Nature* of the 31st May and 16th August 1947, respectively, on the subject of the Raman spectrum of diamond, though all three notes had appeared many months before her paper was sent in for publication.

Then again, we may remark that all the 13 " branches " referred to above cover wide ranges of frequency. In particular, the ranges for the branches 1, 2, 3 and 6 are respectively 140, 430, 1050 and 320 wave-numbers. The positions of the maxima obtained by superposing four smooth curves extending over such wide ranges would depend upon the amplitudes arbitrarily assigned to them. Hence no significance can be attached to any agreement thus artificially secured with the positions of the observed maxima of intensity. It is clearly also not possible by superposing four such curves to reproduce the numerous sharply defined peaks of intensity appearing in the microphotometer record of the spectrogram taken under high resolution (see Fig. 2 above), the positions of which can be determined and specified to within the nearest wave-number. Further, it is clearly impossible by superposing a finite number of such curves to reproduce the steep drops of intensity actually observed in the vicinity of the frequency shifts 2665 and 2176 and shown in Figs. 1 and 3 above.

Thus, in the final analysis, we can state without fear of contradiction that the consequences of the Born-Karman lattice dynamics are wholly incompatible with the experimentally observed behaviour of diamond in the Raman effect. A further serious criticism of a more general nature can also be put forward regarding the approach to the subject made by Max Born and his co-workers. It is evident that for overtones or combinations to appear as frequency shifts in light scattering, the amplitudes of vibration of the atomic systems under consideration should *not* be infinitesimal. For,

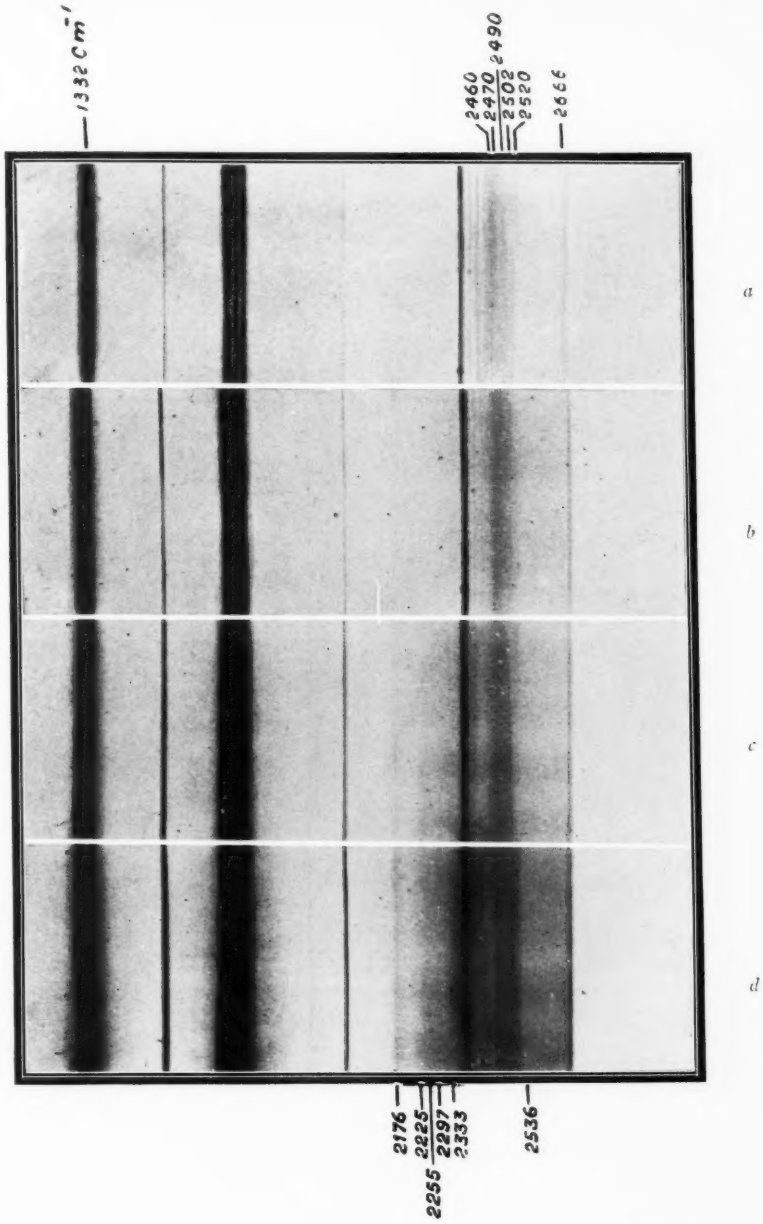

FIG 1 Raman Spectrum of Diamond
(Medium Spectrograph)

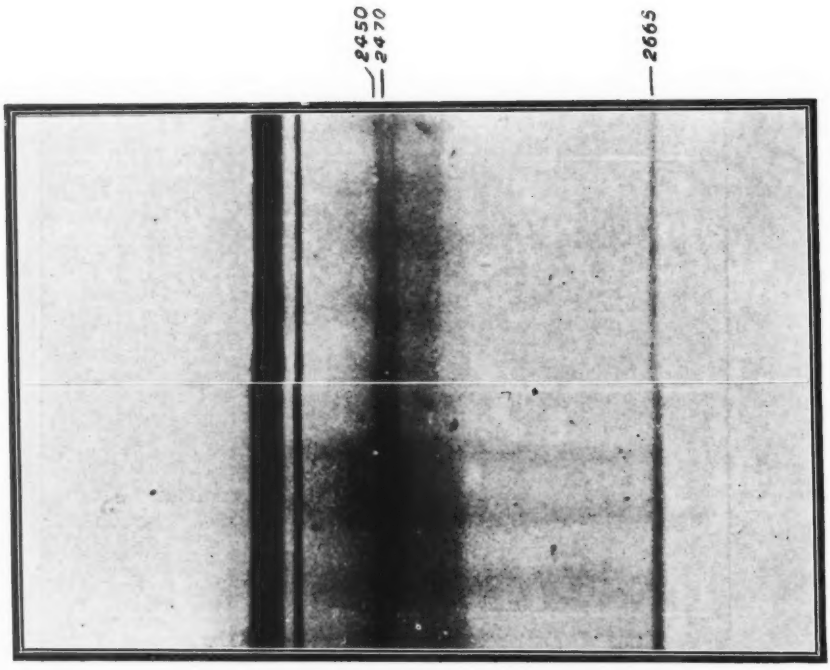

FIG. 2. Second-Order Raman Spectrum of Diamond
(Large Spectrograph)

if they were, the second-order changes in polarisability and the resulting optical effects would vanish. In the Born-Karman lattice dynamics, each individual frequency is regarded as associated with a wave extending through the volume of the crystal. The amplitude of vibration in such a wave would necessarily be infinitesimal. Frequency shifts of the first order might arise as in the case of the coherent reflection of light waves by sound waves (Brillouin effect), but no effect of the second-order would be possible.

We can summarise the situation by stating that, if the basic ideas of the Born-Karman lattice dynamics were valid, no crystal could give frequency shifts in light scattering corresponding to the octaves and combinations of its fundamental frequencies of vibration. Many crystals, however, have been observed to exhibit second-order Raman spectra. It is reasonable to conclude from this that the fundamental ideas of the Born-Karman theory are incompatible with the observed facts of light scattering in crystals.

The author wishes to express his sincere thanks to Prof. R. S. Krishnan for his constant help and encouragement.

Summary

From microphotometric studies of the Raman spectrum of diamond, the distribution of intensity in it has been derived. The spectra themselves exhibit much observable fine structure, including several sharply-defined and intense lines. The intensity curve also exhibits steep drops to zero near the frequency shifts 2176 and 2665 cm.$^{-1}$ These facts are discussed and it is shown that the features mentioned, as also the appearance of second-order Raman spectra generally with crystals, are irreconcilable with the Born-Karman theory of lattice vibrations.

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SOME SIMPLE RELATIONS INVOLVING LEGENDRE'S FUNCTIONS $P_n^m(z)$ AND $Q_n^m(z)$

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INTRODUCTION

GANESH PRASAD* has obtained one relation involving both of Legendre's Associated Functions $P_n^m(z)$ and $Q_n^m(z)$. The problem of getting more relations of this type does not seem to have received the attention of any research worker. In §1 several such relations are obtained by the author, while in §2 he obtains as a few particular cases of these results some new relations involving Legendre's ordinary functions $P_n(z)$ and $Q_n(z)$.

§1

We shall prove that, when n and z are unrestricted and m is a positive integer,

$$P_n^m Q_{n-1}^m - Q_n^m P_{n-1}^m = (-1)^m \frac{(n)_m (n+m)_m}{(n+m)} \tag{I}$$

$$P_n^{m-1} Q_n^m - Q_n^{m-1} P_n^m = (-1)^m \frac{(n)_m (n+m)_m}{(n-m+1)(n+m)} (z^2-1)^{-\frac{1}{2}} \tag{II}$$

$$P_{n+1}^m Q_{n-1}^m - Q_{n+1}^m P_{n-1}^m = (-1)^m \frac{(n)_m (n+m)_m}{(n-m+1)(n+m)} (2n+1)z \tag{III}$$

$$P_n^{m+1} Q_n^{m-1} - Q_n^{m+1} P_n^{m-1} = (-1)^m \frac{(n)_m (n+m)_m}{(n-m+1)(n+m)} \cdot \frac{2mz}{(z^2-1)} \tag{IV}$$

$$P_n^{m-1} Q_{n-1}^m - Q_n^{m-1} P_{n-1}^m = (-1)^m \frac{(n)_m (n+m)_m}{(n-m+1)(n+m)} \cdot z(z^2-1)^{-\frac{1}{2}} \tag{V}$$

$$P_n^{m-1} Q_{n+1}^m - Q_n^{m-1} P_{n+1}^m = (-1)^m \frac{(n)_m (n+m)_m}{(n-m+1)(n+m)} z(z^2-1)^{-\frac{1}{2}} \tag{VI}$$

where $(n)_0 = 1$ and $(n)_m = n(n-1)\ldots(n-m+1)$, $(m = 1, 2, 3, \ldots)$.

* Ganesh Prasad's *Treatise on Spherical Harmonics*, Part II (1932), pp. 87–88.

In order to prove these, the following known recurrence formulæ† will be required.

$$\left.\begin{aligned}(n+m)\,P_{n-1}^{\ m} &= nz\,P_n^{\ m} - (z^2-1)\,P_n'^{m}\\ (n+m)\,Q_{n-1}^{\ m} &= nz\,Q_n^{\ m} - (z^2-1)\,Q_n'^{m}\end{aligned}\right\} \quad (1)$$

$$\left.\begin{aligned}(n-m+1)\,P_{n+1}^{\ m} &= (n+1)\,z\,P_n^{\ m} + (z^2-1)\,P_n'^{m}\\ (n-m+1)\,Q_{n+1}^{\ m} &= (n+1)z\,Q_n^{\ m} + (z^2-1)\,Q_n'^{m}\end{aligned}\right\} \quad (2)$$

$$\left.\begin{aligned}(n-m+1)(n+m)\,P_n^{m-1} &= (z^2-1)^{\frac{1}{2}}\,P_n'^{m} + mz\,(z^2-1)^{-\frac{1}{2}}\,P_n^{m}\\ (n-m+1)(n+m)\,Q_n^{m-1} &= (z^2-1)^{\frac{1}{2}}\,Q_n'^{m} + mz\,(z-1)^{-\frac{1}{2}}\,Q_n^{m}\end{aligned}\right\} \quad (3)$$

$$\left.\begin{aligned}P_n^{m+1} &= (z^2-1)^{\frac{1}{2}}\,P_n'^{m} - mz\,(z^2-1)^{-\frac{1}{2}}\,P_n^{m}\\ Q_n^{m+1} &= (z^2-1)^{\frac{1}{2}}\,Q_n'^{m} - mz\,(z^2-1)^{-\frac{1}{2}}\,Q_n^{m}\end{aligned}\right\} \quad (4)$$

In the above equations (1)–(4), dashes denote derivatives with respect to z.

Substituting from (1)–(4) the values of $P_{n-1}^{\ m}$, $Q_{n-1}^{\ m}$, $P_{n+1}^{\ m}$, $Q_{n+1}^{\ m}$, P_n^{m-1}, Q_n^{m-1}, P_n^{m+1}, Q_n^{m+1} in the left-hand sides of equations (I)–(IV), and denoting $(P_n'^{m}\,Q_n^{\ m} - Q_n'^{m}\,P_n^{\ m})$ by $u_n^{\ m}$, we get

$$(n+m)\begin{vmatrix} P_n^{\ m} & P_{n-1}^{\ m} \\ Q_n^{\ m} & Q_{n-1}^{\ m}\end{vmatrix} = (z^2-1)\,u_n^{\ m};$$

$$(n-m+1)(n+m)\begin{vmatrix} P_n^{m-1} & P_n^{m} \\ Q_n^{m-1} & Q_n^{m}\end{vmatrix} = (z^2-1)^{\frac{1}{2}}u_n^{\ m};$$

$$(n-m+1)(n+m)\begin{vmatrix} P_{n+1}^{\ m} & P_{n-1}^{\ m} \\ Q_{n+1}^{\ m} & Q_{n-1}^{\ m}\end{vmatrix} = (2n+1)\,z\,(z^2-1)\,u_n^{\ m};$$

$$(n-m+1)(n+m)\begin{vmatrix} P_n^{m+1} & P_n^{m-1} \\ Q_n^{m+1} & Q_n^{m-1}\end{vmatrix} = 2mz\,u_n^{\ m};$$

$$(n-m+1)(n+m)\begin{vmatrix} P_n^{m-1} & P_{n-1}^{\ m} \\ Q_n^{m-1} & Q_{n-1}^{\ m}\end{vmatrix} = z\,(z^2-1)^{\frac{1}{2}}\,u_n^{\ m};$$

$$(n-m+1)(n+m)\begin{vmatrix} P_n^{m-1} & P_{n+1}^{\ m} \\ Q_n^{m-1} & Q_{n+1}^{\ m}\end{vmatrix} = z\,(z^2-1)^{\frac{1}{2}}\,u_n^{\ m};$$

But,‡ $u_n^{\ m} = (-1)^m\,(n)_m\,(n+m)_m\,(z^2-1)^{-1}$.

† *loc. cit.*, pp. 83–86.

‡ *loc. cit.*, p. 88. The value of $u_n^{\ m}$ given by Ganesh Prasad is slightly wrong. I have given the correct value of $u_n^{\ m}$ above.

Putting this value of u_n^m in the above equations, we get the relations (I)-(VI).

The following relations can similarly be obtained:—

$$P_n'^m Q_{n-1}^m - Q_n'^m P_{n-1}^m = (-1)^m (n)_m (n+m)_m \frac{n}{(n+m)} \cdot \frac{z}{(z^2-1)} \quad \text{(VII)}$$

$$P_n'^m Q_{n+1}^m - Q_n'^m P_{n+1}^m = (-1)^m (n)_m (n+m)_m \frac{(n+1)}{(n-m+1)} \cdot \frac{z}{(z^2-1)} \quad \text{(VIII)}$$

$$P_n'^m Q_n^{m-1} - Q'^m_n P_n^{m-1} = (-1)^m \frac{(n)_m (n+m)_m}{(n-m+1)(n+m)} \cdot \frac{mz}{(z^2-1)^{3/2}} \quad \text{(IX)}$$

$$P_n^{m+1} Q'^m_n - Q_n^{m+1} P'^m_n = (-1)^m (n)_m (n+m)_m \frac{mz}{(z^2-1)^{3/2}} \quad \text{(X)}$$

§2

Some particular cases of the relations just proved may now be considered.

For example, putting $m=2$ in (II) and making use of the definitions of $P_n^m(z)$ and $Q_n^m(z)$, we get

$$P_n' Q_n'' - Q_n' P_n'' = \frac{n(n+1)}{(z^2-1)^2}. \quad \text{(i)}$$

Again, putting $m=1$ in (III), (V) and (VI) respectively, we get

$$P_{n+1}' Q_{n-1}' - Q_{n+1}' P_{n-1}' = -\frac{(2n+1)z}{(z^2-1)} \quad \text{(ii)}$$

$$P_n Q_{n-1}' - Q_n P_{n-1}' = -\frac{z}{(z^2-1)} \quad \text{(iii)}$$

$$P_n' Q_{n-1} - Q_n' P_{n-1} = \frac{z}{(z^2-1)} \quad \text{(iv)}$$

In conclusion, I wish to thank the referee for his helpful criticism.

CHEMOTHERAPY OF BACTERIAL INFECTIONS

XIII. Synthesis of Unsymmetrical Diphenylsulphones

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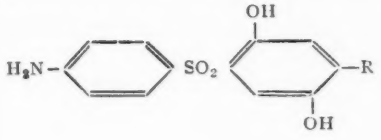
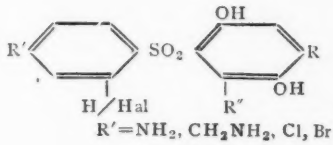
While investigating the chemotherapeutic agents in the sulphone group, Walker[1] synthesised 2:5-dihydroxy-4′-aminodiphenylsulphone (I, R = H) and derivatives and showed that the compound (I, R = H) approached sulphathiazole in its activity against *P. pestis* and *B. coli* and slightly better than sulphathiazole against the organisms belonging to the *Clostridia* group. When locally applied to mice infected with *Clostridium septicum*, it was reported to show marked effect and it had low chronic toxicity when fed to



(I)



R′ = NH_2, CH_2NH_2, Cl, Br

(II)

mice. This shows that the substitution of the amino group in one benzene ring by the hydroxyl groups produced compounds of greater degree of activity, and in addition lower toxicity. So we decided to investigate compounds of general formulæ I and II. In introducing further substituents in one benzene ring, we selected the halogen atoms and the methylamino group because sulphanilamido derivatives with these substituents have been shown to be not reversed as far as their therapeutic activity is concerned by *para*-aminobenzoic acid.[2]

The requisite sulphone derivatives were prepared by the Hinsberg reaction[3] which consisted in reacting the sulphinic acids with benzoquinone derivatives. In this work, we selected *p*-acetaminobenzenesulphinic acid, *p*-acetaminomethylbenzenesulphinic acid, *p*-chlorobenzenesulphinic acid, *p*-bromobenzenesulphinic acid and benzenesulphinic acid as the representative sulphinic acids. Benzoquinone, 2-chlorobenzoquinone, 2-bromobenzoquinone, and 2:5-dichlorobenzoquinone were the representative quinones. The nineteen sulphones obtained are listed in the table.

The structure of the sulphones obtained from benzoquinone or the 2:5-dichlorobenzoquinone is unambiguous because of the symmetrical

TABLE I

Sl. No.	Name of Compound	Formula	M. P. °C.	Analysis %	
				Found	Require
1	2:5–Dihydroxy-3:6-dichloro-4′-acetaminodiphenylsulphone	$C_{14}H_{11}O_5NSCl_2$	246° dec.	Cl, 18·8 N, 3·5	18·9 3·7
2	2:5-Dihydroxy-3:6-dichloro-4′-aminodiphenylsulphone hydrochloride	$C_{12}H_{10}O_4NSCl_3$	200–02° dec.	Cl, 28·9	28·7
3	2:5-Dihydroxy-4(?)-bromo-4′-acetaminodiphenylsulphone	$C_{14}H_{12}O_5NSBr$	262° dec.	Br. 20·9	20·7
4	2:5-Dihydroxy-4(?)-bromo-4′-aminodiphenylsulphone	$C_{12}H_{10}O_4NSBr$	180–82°		
5	2:5-Dihydroxy-4′-acetamino-methyldiphenylsulphone	$C_{15}H_{15}O_5NS$	238°	N, 4·5	4·4
6	2:5-Dihydroxy-4′-aminomethyl-diphenylsulphone-hydrochloride	$C_{13}H_{14}O_4NSCl$	247–48° d.	Cl, 11·6	11·3
7	2:5-Dihydroxy-4′-aminomethyl-diphenylsulphone	$C_{13}H_{13}O_4NS$	172–74°	N, 4·8	5·0
8	2:5 Dihydroxy-4(?)-chloro-4′-acetaminomethyldiphenylsulphone	$C_{15}H_{14}O_5NSCl$	210–11°	Cl, 10·2	10·0
9	2:5-Dihydroxy-4(?)-chloro-4′-aminomethyldiphenylsulphone-hydrochloride	$C_{13}H_{13}O_4NSCl_2$	245° d.	Cl, 20·1	20·3
10	2:5-Dihydroxy-4(?)-chloro-4′-aminomethyldiphenylsulphone	$C_{13}H_{12}O_4NSCl$	230–31°	Cl, 11·0	11·3
11	2:5-Dihydroxy-3:6-dichloro 4′-acetaminomethyldiphenylsulphone	$C_{15}H_{13}O_5NSCl_2$	211–12° d.	Cl, 18·5	18·2
12	2:5-Dihydroxy-3:6-dichloro-4′-aminomethyl-diphenylsulphone hydrochloride	$C_{13}H_{12}O_4NSCl_3$	Decomposes above 235	Cl, 27·8	27·7
13	2:5-Dihydroxy-3:6-dichloro-4′-aminomethyldiphenylsulphone	$C_{13}H_{11}O_4NSCl_2$	Decomposes above 195	Cl, 20·0	20·4
14	2:5-Dihydroxy-2′:5′-dichlorodiphenylsulphone	$C_{12}H_8O_4SCl_2$	188-90°	Cl, 22·1	22·3
15	2:5-Dihydroxy-4(?)-chloro-2′:-5′-dichlorodiphenylsulphone	$C_{12}H_7O_4SCl_3$	135°	Cl, 30·3	30·1
16	2:5-Dihydroxy-3:6:2′:5′-tetrachlorodiphenylsulphone	$C_{12}H_6O_4SCl_4$	197-98°	Cl, 36·2	36·6
17	2:5-Dihydroxy-4(?) bromo-2′:5′-dichlorodiphenyl-sulphone	$C_{12}H_7O_4SCl_2Br$	128–30		
18	2:5-Dihydroxy-4′-chlorodiphenylsulphone	$C_{12}H_9O_4SCl$	205–06°	Cl, 12·4	12·5
19	2:5-Dihydroxy-4′-bromo-diphenylsulphone	$C_{12}H_9O_4SBr$	211–12°	Br. 24·4	24·3

distribution of the substituents in the ring. In the case of the sulphones prepared from monosubstituted benzoquinone however, there are three possibilities because the halogen atom can occupy three possible positions. Under the experimental conditions employed, we have isolated only one compound and for the compounds, we assign the structure (I) as the most probable.

A number of compounds from among those synthesised were tested for activity against *P. gallinaceum* in mosquitoes for the prophylactic activity and but they were found to be devoid of activity. The results of testing them in bacterial infections will be reported in due course.

Experimental

The sulphinic acids were prepared by the general method of Bere and Smiles[4] by the sulphite reduction of the sulphochlorides. The modification of the sulphite reduction by the use of sodium carbonate instead of sodium hydroxide as described by Short and Koebner[5] resulted in better yields and purer products. The alkali metal salts of the sulphinic acids were more stable than the free acids, this being particularly true of *p*-chloro and *p*-bromobenzene sulphinic acids. The decomposition of these acids was hastened by even traces of acids.

2: 5-*Dihydroxy*-3:6-*dichloro*-4'-*acetaminodiphenylsulphone*.—*p*-Acetaminobenzenesulphinic acid (5 g.) was suspended in a mixture of ethanol (50 c.c.) and water (5 c.c.) and cooled in an ice-bath. To the cooled suspension was added powdered 2: 5-dichlorobenzoquinone (4 g.) and the mixture vigorously shaken. Decolorisation took place with the suspended reactants going into a practically colourless solution and shortly thereafter white crystals began to separate. The contents were then heated on the steam-bath for about fifteen minutes, cooled and filtered. The solid was washed with dilute ethanol and dried (yield, 7·0 g., m.p. 246° dec.). On crystallisation from dilute ethanol, it had m.p. 246° (dec.).

2: 5-*Dihydroxy*-3:6-*dichloro*-4'-*aminodiphenylsulphone hydrochloride*.—The above described acetyl compound (4 g.) was suspended in a mixture of ethanol (20 c.c.), hydrochloric acid (20 c.c.) and water (20 c.c.) and the mixture refluxed for about six to seven hours when the solid went completely into solution. The solution was clarified (charcoal), filtered hot and kept in an ice-box. The crystals that had separated were filtered and dried (yield, 3·2 g., m.p. 190–93°). It was recrystallised from dilute ethanol.

The compounds listed in the table were prepared by the above described general method.

Summary

Nineteen diarylsulphones of general formulæ (I) and (II) listed in the table have been synthesised by the Hinsberg reaction, with a view to study them for their action against gram positive anaerobes.

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ON SOME NEW RECURRENCE FORMULÆ FOR CUMULANTS OF MULTIVARIATE MULTINOMIAL DISTRIBUTIONS

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Wishart[1] has found the cumulants of multivariate multinomial distributions in terms of the marginal probabilities. Here I shall find new recurrence formulæ of cumulants and show that the cumulant of any order may be expressed as prolynomials of cumulants of lower order.

We know[2] that if K is the cumulant generating function of the multinomial distribution $\frac{S\,!}{x_0\,!\,x_1\,!\,\ldots x_n\,!}\,p_0^{x_0}\,p_1^{x_1}\,\ldots\,p_n^{x_n}$

then

$$K\ldots1\ldots=\left(\frac{\partial K}{\partial t_i}\right)_{t_i=0}=\frac{Sa_i}{1+\Sigma a_i},\quad\text{where}\quad a_i=\frac{p_i}{p_0}.$$

Hence

$$K\ldots2\ldots=\left(\frac{\partial^2 K}{\partial t_i^{\,2}}\right)_{t_i=0}=\frac{Sa_i}{1+\Sigma a_i}-\frac{Sa_i^{\,2}}{[1+\Sigma a_i]^2}$$

$$K\ldots1\ldots-\frac{1}{s}\,K^2\ldots1\ldots \tag{1}$$

Now[3]

$$K\ldots3\ldots=a_i\frac{\partial}{\partial a_i}K\ldots2\ldots=K\ldots2\ldots-\frac{2}{s}K\ldots1\ldots x\,K\ldots2\ldots$$

Hence

$$K\ldots3+u\ldots=K\ldots2+u\ldots-\frac{2}{s}\sum_{v=0}^{u}{}^{u}C_v\,K\ldots u-v+1\ldots X$$

$$K\ldots2+v\ldots \tag{2}$$

Again

$$K_1\ldots1\ldots=\left(\frac{\partial^2 K}{\partial t_i\,\partial t_i)}\right)_{t_i=0=t_1}=-\frac{Sa_ia_1}{[1+\Sigma a_i]^2}$$

$$=a_1\frac{\partial}{\partial a_1}K\ldots1\ldots=-\frac{1}{s}K_1\ldots X\;K\ldots1\ldots$$

Hence

$$\mathrm{K}r_1\ldots 3+p\ldots=\mathrm{K}r_1\ldots 2+p\ldots-\frac{2}{s}\Big[\sum_{r=0}^{p}{}^{p}\mathrm{C}r\Big\{\sum_{u=0}^{r_1}{}^{r_1}\mathrm{C}_u\mathrm{X}$$

$$\mathrm{K}r_1-u\ldots p-r+1\times\mathrm{K}_u\ldots 2+r\Big\}\Big] \tag{3}$$

Similarly

$$\mathrm{K}r_1r_2\ldots 3+p\ldots=\mathrm{K}r_1r_2\ldots 2+p\ldots$$

$$-\frac{2}{s}\Big[\sum_{r=0}^{p}{}^{p}\mathrm{C}_r\sum_{0}^{r_1}{}^{r_1}\mathrm{C}_u\Big\{\sum_{0}^{r_2}{}^{r_2}\mathrm{C}_v\,\mathrm{K}r_1-u\,r_2-v\cdots p-r+1\,\mathrm{X}$$

$$\mathrm{K}uv\cdots 2+r\Big]\text{ and so on.}$$

Particular cases are

$$\mathrm{K}\ldots 2\ldots=\mathrm{K}\ldots 1\ldots\left[1-\frac{\mathrm{K}\ldots 1\ldots}{s}\right]$$

$$\mathrm{K}\ldots 3\ldots=\mathrm{K}\ldots 1\ldots\left[1-\frac{\mathrm{K}\ldots 1\ldots}{s}\right]\left[1-\frac{2\,\mathrm{K}\ldots 1\ldots}{s}\right]$$

$$\mathrm{K}\ldots 4\ldots=\mathrm{K}\ldots 1\ldots\left[1-\frac{\mathrm{K}\ldots 1}{s}\right]\left[1-\frac{6}{s}\mathrm{K}\ldots 1\ldots\right.$$

$$\left.+\frac{6}{s^2}\mathrm{K}^2\ldots 1\ldots\right] \tag{5}$$

Again

$$\mathrm{K}_1\ldots 2\ldots=a_1\frac{\partial}{\partial a_1}\,\mathrm{K}\ldots 2\ldots=\mathrm{K}_1\ldots 1\ldots\left(1-\frac{2}{s}\mathrm{K}\ldots 1\ldots\right)$$

Similarly

$$\mathrm{K}_2\ldots 2\ldots$$

$$=\mathrm{K}_1\ldots 1\ldots\left(1-\frac{2}{s}\mathrm{K}_1\ldots\right)\left(1-\frac{2}{s}\mathrm{K}\ldots 1\ldots\right)-\frac{2}{s}\mathrm{K}_1{}^2\ldots 1 \tag{6}$$

and so on.

Let

$$\mathrm{D}_i=a_i\frac{\partial}{\partial a_i}.\quad\text{Then }\mathrm{K}r_1+1\,r_2+1\ldots r_n+1$$

$$=\mathrm{D}_1{}^{r_1}\mathrm{D}_2{}^{r_2}\ldots\mathrm{D}_n{}^{r_n}\,\mathrm{K}_{11\cdots 1}$$

Let

$$a_0=1+\Sigma a_i$$

Then

$$a_0\,\mathrm{K}\ldots 1\ldots=\mathrm{S}a_i$$

Hence

$$a_0\,\mathrm{K}\ldots 2\ldots+a_i\mathrm{K}\ldots 1\ldots=\mathrm{S}a_i$$

Generally

$$a_0 \mathrm{K}\ldots r_i\ldots + {}^{r_i-1}\mathrm{C}_1 a_j \mathrm{K}\ldots r_i-1\ldots + {}^{r_i-1}\mathrm{C}_2 a_i \mathrm{K}\ldots r_i-2\ldots + a_i \mathrm{K}\ldots 1\ldots = \mathrm{S}a_i \tag{7}$$

Let

$p_i q_i = \mathrm{C}_i$, $q_i = \mathrm{I}_i + p_i$ Then $\mathrm{K}\ldots r_i + 1\ldots$

$= \mathrm{C}_i \dfrac{\partial \mathrm{K}\ldots r_i}{\partial p_i}$. Now $\dfrac{\partial \mathrm{C}_i}{\partial p_i} = q_i - p_i = \mathrm{I}_i$ and $\dfrac{\partial \mathrm{I}_i}{\partial p_i} = -2$

$\mathrm{I}_i^2 = 1 - 4\mathrm{C}_i$

Since

$\mathrm{K}\ldots 2\ldots = \mathrm{SC}_i$. Let us assume $\mathrm{K}\ldots r_i\ldots = \mathrm{S}f(\mathrm{C}_i)$.

Then

$\mathrm{K}\ldots r_{i+1} = \mathrm{SC}_i \mathrm{I}_i f'(\mathrm{C}_i)$

$\mathrm{K}\cdots r_{i+2}\cdots = \mathrm{SC}_i'(1 - 6\mathrm{C}_i) f'(\mathrm{C}_i) + \mathrm{SC}_i^2 (1 - 4\mathrm{C}) f''(\mathrm{C}_i)$ (8)

With the help of the formulæ (8) we can calculate

$\mathrm{K}\ldots r_i\ldots$ for all the values of r_i.

Again

$$\mathrm{K}\ldots r_{i+1} r_j\ldots = p_i q_i \frac{\partial}{\partial p_i} \mathrm{K}\ldots r_i r_j - p_i p_j \frac{\partial \mathrm{K}\ldots r_i r_j}{\partial p_i}$$

If

$\mathrm{K}\ldots r_i r_j = sf(\mathrm{C}_{ij}, \mathrm{C}_i, \mathrm{C}_j)$

$$\mathrm{K}\ldots r_{i+1} r_i\ldots = s\mathrm{C}_i \left[\frac{df}{\partial \mathrm{C}_i} \mathrm{I}_i + p_j \frac{\partial f}{\partial \mathrm{C}_{ii}}\right]$$

$$- s\mathrm{C}_{ij}\left[p_i \frac{\partial f}{\partial \mathrm{C}_{ij}} + \mathrm{I}_i \frac{\partial f}{\partial \mathrm{C}_i}\right] \tag{9}$$

As $\mathrm{K}\ldots 11 = -\mathrm{S}p_i p_j$. We can calculate the values of $\mathrm{K}\ldots r_i r_j\ldots$ with the help of formulæ (9). Similarly we can find $\mathrm{K}r_1 r_2 \cdots r_n$.

Corresponding result exist in which the former negative signs are replaced by positive in case of negative binomial distribution.

II

Let us consider the bivariate binomial distribution of the Bernoulle's kind.

We know $a_{00}\mathrm{K}_{10} = \mathrm{S}(a_{10} + a_{11})$

$$\mathrm{K}_{20} = \left(a_{10} \frac{\partial}{\partial a_{10}} + a_{11} \frac{\partial}{da_{11}}\right), \mathrm{K}_{10} \text{ where } a_{00} = 1 + a_{01} + a_{11} + a_{10}$$

Hence

$$a_{00}K_{20} + (a_{10} + a_{11})\, K_{10} = S\,(a_{10} + a_{11})$$

$$a_{00}K_{30} + 2\,(a_{10} + a_{11})\, K_{20} + (a_{10} + a_{11})\, K_{10} = S\,(a_{10} + a_{11})$$

and so on.

Again

$$K_{r_1 r_2} = D_1^{r_1} D_2^{r_2} K_{11} \text{ where } D_1 = a_{10} \frac{\partial}{\partial a_{10}} + a_{11} \frac{\partial}{\partial a_{11}}$$

and

$$D_2 = a_{01} \frac{\partial}{\partial a_{01}} + a_{11} \frac{\partial}{\partial a_{11}}.$$

Results similar to (1), (2), (3) can be found out. We can also find similar results in case of multivariate Bernoulle distribution.

Corresponding results, in case of multinomial Pascal distribution exist.

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ULTRASONIC VELOCITIES IN LIQUIDS BY A NEW METHOD

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(Communicated by Prof. S. Bhagavantam, F.A.Sc.)

1. Introduction and Experimental Details

In a recent communication,[1] the author has proposed a simple and new method for determining the velocities of ultrasonic waves in liquids which is based on a principle similar to the wedge method developed by Bhagavantam and Bhimasenachar[2] for elastic constants of solids. While studying the frequency spectrum of different types of wedges, the author has come across a curious result that continuous ranges of ultrasonic waves generated by a wedge exhibit sharp maxima when communicated to the diffraction cell through a thin uniform liquid film. This enabled a new method to be devised for measuring the ultrasonic velocities in liquids using the liquid in the form of a plate and determining its resonance frequencies.

In this method a small liquid cell is made out of a brass annular disc of uniform thickness (about 2 mm.) by closing both sides with two thin cover glass slips. The space enclosed by the cover slips can be completely filled up by about 0·25 c.c. of liquid which is introduced through a side hole provided in the brass disc. The liquid spreading in between the cover slips forms, as it were, a liquid plate of uniform thickness. Ultrasonic waves generated by a suitable tourmaline wedge giving a range of 3–7 Mcs./sec. are transmitted through this liquid cell and communicated to water contained in a glass trough. The ultrasonic wave thus transmitted through the liquid plate sets up an ultrasonic grating in the water contained in the glass trough whose diffraction effect is observed with the usual arrangement. The transmission maxima of the liquid plate are determined by observing the maxima in the intensity of the diffraction pattern. These maxima which correspond to the resonance frequencies of the liquid plate will enable the estimation of the fundamental resonance frequency. The fundamental resonance frequency of the liquid plate being of a low order (about 0·3 Mcs./sec.) a good number of transmission maxima are observed using a wedge of a short frequency range enabling a reasonably accurate determination of the fundamental frequency. All observations are made at constant temperature and the oscillator employed is of the usual Hartley type covering a wide range

of frequencies which are measured with a standard Philips Heterodyne Wavemeter using a rectifier and audioamplifier for hearing the beat note.

2. Results

Table I gives some of the large number of transmission maxima observed in the case of water along with the order of harmonic that is excited and the fundamental frequencies deduced from them.

Table I

Resonance Frequencies of water plate in Mcs./sec.	Order of harmonic	Fundamental frequency in Mcs./sec.
4·62	15	0·308
4·91	16	0·307
5·20	17	0·306
5·51	18	0·306
5·79	19	0·305
6·08	20	0·304
6·38	21	0·304

The fundamental frequency thus evaluated, though fairly constant, clearly indicated a slight dependence on the transmission frequency. This effect has to be interpreted as due to the size of the container but not as an evidence of dispersion. Detailed investigations are in progress regarding the size effect of the container by taking various sizes of liquid cells. In fact, it is found that there is not much of a variation in the value of the fundamental beyond 6 Mcs./sec. Taking the value obtained at the high frequencies as the true fundamental, the velocities are calculated in the usual manner. There is also slight evidence of damping of the liquid plate by the water contained in the glass trough. This can be avoided by resorting to an electrical method for detecting and amplifying the transmitted ultrasonic beam. This would also enable the setting of the oscillator for the maximum intensity of the diffraction pattern more precisely than by the visual judgment of its intensity.

Results obtained for the velocities by a number of transparent and opaque liquids are given in Table II along with the values reported in the literature. Agreement is satisfactory in spite of the probable sources of error due to damping and size effect.

TABLE II

Liquid	Fundamental frequency (Mcs./sec.)	Velocity calculated in metres per sec. at 30° C.	Velocities obtained by other methods at (23°–27° C.)	References
Glycerine ..	0·390	1950	1986	3
Water ..	0·304	1520	1500	3
Mercury ..	0·285	1425	1440	4
Toluene ..	0·260	1300	1300	3
Ethyl alcohol ..	0·231	1155	1150	3
Carbon tetrachloride ..	0·181	905	930	3

3. DISCUSSION

The capacity of the liquid cell used in the above investigation is only 0·25 c.c. and thus velocities in liquids available even in such small quantities can be determined. The method is simple and rapid being particularly suitable for opaque liquids for which the only method of obtaining velocities at high frequencies is by the pulse technique. The investigation of dispersion of sound velocity at very high frequencies in liquids having high absorption coefficient is not possible by the Debye-Sears' method in view of the feeble intensity of diffraction pattern as well as the temperature disturbance. This method can be used with advantage in such cases as the amount of ultrasonic energy absorbed will not be considerable for small quantities of liquids. The possibility of extending this method for study of dispersion is being investigated.

4. SUMMARY

A new method of determining velocities in transparent and opaque liquids using ultrasonic frequencies over a wide range has been described. Results obtained for a number of organic and inorganic liquids are given. They compare well with values reported earlier in the literature. Only a small quantity of 0·25 c.c. is all that is required and hence the method is particularly suitable for liquids available in very small quantities. The possibility of extending this method for study of dispersion in a variety of liquids is envisaged.

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STUDIES ON PLANT MUCILAGES

Part III. Mucilage from the Tubers of *Curculigo orchioides*

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In continuation of the work in progress in these laboratories on plant mucilages, the examination of the tubers of *Curculigo orchioides* Gaertn. has been undertaken. *Curculigo orchioides* is a small herbaceous plant growing in the hotter regions of India and Ceylon. The tuberous root of this plant, which is called *Kalimusli* in Hindi, is largely used in the Ayurvedic and Unani systems of medicine as a tonic and for piles and diarrhœa.

The fresh roots are soft and pliable, but become hard and brittle on drying. When dried roots are powdered and passed through a 80-mesh sieve, most of the fibrous bark is retained by the sieve, while the core powder passes through. The following are the results of a proximate analysis of the core powder:—

Moisture	10·42 per cent.
Fat	1·92 ,,
Colouring matter	3·28 ,,
Proteins	9·81 ,,
Fibre	15·70 ,,
Nonfibre carbohydrates	53·20 ,,
Inorganic matter (by difference)	5·67 ,,
Ash content	5·51 ,,

Carbohydrates are, therefore, the main constituent of the tubers. Their further examination has shown that they are composed of free sugars (7·56 per cent. on the weight of the air-dried core powder), mucilages (8·12 per cent.), hemicelluloses (20·51 per cent.), and other polysaccharides (17·01 per cent.). The free sugars, which are extractable with 70 per cent. alcohol, are found to be composed of only xylose and glucose. The residue, left after the extraction of the free sugars, when treated with warm water, yields a somewhat sticky viscous solution, which on treatment with alcohol, precipitates a greyish substance. The latter, unlike hemicelluloses, undergoes hydrolysis with difficulty to simple sugars and uronic acid and hence

belongs to the class of mucilages. The constituent sugars are mannose and glucose, while the uronic acid is found to be glucuronic acid. Quantitative estimations have shown that mannose, glucose and glucuronic acid are present in the ratio of 6 : 9 : 10 in the mucilage molecule.

Experimental

Composition of the Root Powder.—The tubers were obtained from Sambalpur circle (Orissa State). After drying they were ground in a pulverizer and passed through a 80-mesh sieve. The bark was retained by the sieve, while the inner core powder passed through it. The powder thus obtained was a little darkish brown in colour. Its proximate analysis was carried out according to standard methods,[1] and the results have already been presented under the theoretical introduction. The ash contained Na^{+}, K^{+}, Ca^{++}, Mg^{++}, and Fe^{+++} as the basic radicals and CO_3^{--}, SO_4^{--}, and PO_4^{---} as the acid radicals. Some silica was also present.

Estimation and Identification of Free Sugars.—The root powder (50 g.) was taken in a big soxhlet extractor and extracted with 500 c.c. of absolute alcohol till the extract removed no more of the colouring matter. After the removal of colouring matter, the extraction was continued with 70 per cent. alcohol for six hours. When the extraction was over, alcohol was distilled off from the extract, the aqueous solution was clarified with alumina cream, the volume was made up to a known volume and the sugars analysed both qualitatively and quantitatively. The solution contained only glucose and xylose. Glucose was detected by the formation of the characteristically crystalline phenyl osazone, melting at 204°–06° and the diphenyl hydrazone melting at 161°. The presence of xylose was established by the formation of the characteristic boat-shaped crystals of cadmium bromide-cadmium xylonate on oxidation with bromine and treatment with cadmium carbonate. Further, when a small portion of the sugar solution was evaporated to dryness and the dry product treated with benzaldehyde and methanolic hydrogen chloride, dimethylacetal of dibenzylidene *d*-xylose separated, confirming the presence of xylose.[2] The total sugars were estimated according to the method of Allihn and were found to be 7·56 per cent. Xylose was determined by estimating the amount of furfural liberated, when the sugar solution was boiled with 12 per cent. hydrochloric acid at 175°–80° and was found to be 25·68 per cent.

Isolation of the Mucilage.—The root powder (50 g.) was treated with warm water (1 l) for 3 hours. After removal of the suspended impurities by filtration through silk and subsequent centrifuging a moderately viscous solution was obtained. It was poured with stirring into alcohol (2 l)

containing a few c.c. of concentrated hydrochloric acid. The mucilage separated out as a greyish mass. It was again dissolved in water and reprecipitated from alcohol containing a little hydrochloric acid. The process was repeated thrice and the ash content was determined every time to indicate the purity. The final product, which was fairly free from ash, was dehydrated by tituration first with warm absolute alcohol and then with ether. The resultant powder was finally dried in a vacuum desiccator. The yield was 4·06 g. On powdering it looked greyish and was amorphous under the microscope. Its solution was faintly acidic and did not reduce Fehling's solution either in the cold or on heating. In 0·5 per cent. solution in water it had a specific rotation of 99·6° at 30°.

Estimation of Uronic Anhydride.—This was done according to the method of Dickson, Otterson and Link[3] by boiling 3 g. of the mucilage with 100 c.c. of 12 per cent. hydrochloric acid (sp. gr. 1·06). Calculated on the basis of dry material, the mucilage contained 39·56 per cent. of the anhydride.

Hydrolysis of the Mucilage.—The purified air-dried mucilage (3 g.) was boiled under reflux with 200 c.c. of 5 per cent. sulphuric acid for four hours. The temperature was gradually raised to the boiling point to avoid any local heating and consequent charring. The resultant hydrolyzate was dark brown in colour due to the formation of furfuraldehyde from the liberated uronic acid. However, partial decomposition of uronic acid was minimized, if not altogether eliminated, by conducting the hydrolysis at the temperature of boiling water-bath (98°) for a long time (18 hours) and subsequently on a wire-gauze for 2 hours. The latter direct heating was to ensure the completion of the hydrolysis. Under these conditions, the uronic acid did not seem to undergo any appreciable decomposition. For the characterization of the uronic acid and the other products, the hydrolyzate, about 200 c.c., was neutralized in the hot with barium carbonate, the precipitated barium sulphate was filtered off and the filtrate concentrated to 100 c.c. under vacuum. On adding 300 c.c. of alcohol to the concentrate, the barium salt of the uronic acid separated out. After filtration, the residue and the filtrate were examined separately for the identification of the uronic acid and the sugars respectively.

Nature and Relative Proportion of the Sugars.—From the filtrate alcohol was distilled off and the residuary aqueous solution was made up to 200 c.c. in a standard flask. When a small part of the sugar solution was treated with well-cooled phenylhydrazine solution in acetic acid, mannose phenylhydrazone melting at 188° separated out. The mixture was left overnight in a frigidaire to completely precipitate the hydrazone and the latter filtered

off. The filtrate, after the addition of a little more phenylhydrazine acetate, was heated on a water-bath to see if any osazone would separate out. In about fifteen minutes, phenyl glucosazone crystallized out with its characteristic structure and melting point (204°–06°). The sugar solution did not respond to Pinoff's and Seliwanoff's tests[4, 5] indicating the absence of fructose. It did not produce any mucic acid on oxidation with nitric acid showing that galactose was absent. Tests for pentoses were also negative. Hence mannose and glucose were the only sugars present in the hydrolyzate.

Quantitatively the total sugars in the solution were estimated according to Allihn's method. Mannose was determined as follows (method of Bourquelot and Herissey).[6] 50 c.c. of the sugar solution was concentrated to about 20 c.c. and treated in the cold with a well-cooled mixture of 2 c.c. of phenylhydrazine, 1 c.c. of glacial acetic acid and 6 c.c. of water. The mixture was allowed to stand with occasional shaking for 4 hours at a temperature below 10°. The precipitated hydrazone was filtered in a glass-sintered crucible, washed with 10 c.c. of absolute alcohol and 10 c.c. of ether. The hydrazone was dried at 100° for half an hour in a steam oven and weighed. The amount of the hydrazone, when multiplied by 0·666, gave the amount of mannose. The latter was found to be 40·13 per cent. of the sugars. Hence mannose and glucose were present in the ratio of 2 : 3.

Nature of the Uronic Acid.—The barium uronate obtained was purified by repeated precipitations from aqueous solution by means of alcohol. The purified salt contained 25·37 per cent. of barium, barium uronate requiring 26·40 per cent. of the metal. On oxidation with nitric acid (1·15 d.) it did not produce any mucic acid, thereby indicating that it was not galacturonic acid. In aqueous solution (c = 0·4 per cent.), the salt showed a specific rotation of + 17·76° at 25°, indicating that it might be barium glucuronate (the specific rotation of barium glucuronate is reported to be + 15·0° at 19°).[7] For confirmation, the free uronic acid was liberated from the barium salt by treatment with just the required amount of sulphuric acid, and its specific rotation determined. It was found to be + 37·74° at 25° (glucuronic acid has a specific rotation of + 35·2° at 23°).[8] Hence the barium salt was concluded to be barium glucuronate in a somewhat impure state.

Relative Proportion of the Sugars and the Uronic Acid in the Mucilage Molecule.—As already seen, the mucilage contained nearly 40 per cent. of uronic acid and 60 per cent. of sugars. The latter were composed of mannose and glucose in the molecular ratio of 2 : 3. Since the uronic acid and the sugars are nearly of the same molecular weight, the mucilage

molecule may be said to be constituted from mannose, glucose and glucuronic acid in the molecular ratio of 6 : 9 : 10.

Summary

The mucilage from the tubers of *Curculigo orchioides* Gaertn. is constituted from mannose, glucose and glucuronic acid in the molecular ratio of 6 : 9 : 10. It is present to an extent of 8·12 per cent.

The results of a proximate analysis of the root powder are also given.

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FARADAY EFFECT AND BIREFRINGENCE—I

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1. Introduction

It is well known that the presence of birefringence in a solid, both accidental and inherent, considerably decreases the magnitude of its magneto-optic rotation (Schutz, 1936). In consequence, very great care has to be exercised in selecting perfect crystals for the measurement of Faraday rotation. It was therefore considered that an investigation of the influence of birefringence on the Faraday effect in a solid would be of some interest. Although the complete theory of magnetic and optical rotation in birefringent solids has been worked out (Chauvin, 1890; Wiener, 1888; Pockels, 1906) this particular problem of the magnitude of the decrease in the rotation has not been specifically treated before. In the present investigation the general theories have been used to derive simple expressions correlating the decrease in the magnetic rotation with birefringence. The preliminary report of this has already been published in *Current Science* (Ramaseshan and Chandrasekharan, 1951). These expressions have been verified by experiments on strained glass and strained plastics. It is found that birefringences corresponding to path retardations of the order of $\lambda/30$ for the total length of the solid do not affect the magnetic rotation by more than 1%. The rotation actually becomes zero for a path retardation of about $\lambda/2$ and has a negative value when it is between $\lambda/2$ and λ. Further, it is found that the Verdet constant in birefringent solids can be measured accurately, provided thin specimens are taken such that the total birefringence is not very large. In fact the decrease in the Faraday rotation in a strained solid can itself be used to calculate the birefringence very accurately.

2. Rotation for Low Birefringence

When plane polarised light is incident on an isotropic solid placed in a magnetic field, it is split up into two circular vibrations of opposite senses which travel with different velocities inside the medium. Since these two vibrations are coherent, they combine at every point in the medium to produce a plane vibration which is rotated with respect to the plane of polarisation of the incident light, the rotation increasing directly as the thickness

traversed. By measuring the value of the rotation ρ for the whole thickness t of the solid for a known field, the Verdet constant of the substance can be calculated. Let us now assume that the isotropic solid is made birefringent by the application of a stress. In this case the incident plane polarised light splits up into two elliptic vibrations of opposite senses lying crossed to each other, which travel with different velocities. These being coherent, they combine at every point to produce an elliptic vibration whose major axis is rotated with respect to the plane of polarisation of the incident light. The magnitude of the rotation of the major axis (ψ) depends on the thickness and the birefringence of the solid. It is possible to measure the angle ψ very accurately with a half shade if the ellipticity of the emergent light is not very large. ψ can be considered to be the apparent rotation, and the so-called decrease in the rotation in a strained solid is due to the fact that ψ is less than ρ, if the incident light is polarised parallel to a principal direction, as would happen if the solid were originally set for minimum restoration of light under crossed nicols. However, this is not always true and the apparent rotation would actually increase if the incident light is polarised at 45° to the principal directions. We shall consider only the former case as measurements are best made in that setting. An expression connecting ψ with the birefringence and the rotation would enable one to calculate the true Verdet constant of a stressed or birefringent solid.

Let δ_0 be the phase retardation per unit length in the absence of rotation and ρ_0 the rotation per unit length when there is no birefringence. Then the phase retardation per unit length Δ_0 between the two elliptic vibrations that are propagated unchanged inside the anisotropic medium is given by

$$\Delta_0 = \sqrt{\delta_0^2 + (2\rho_0)^2} \tag{1}$$

and the ratio of the axes of the ellipse is given by $\tan \gamma$, where

$$\tan 2\gamma = 2\rho_0/\delta_0 \tag{2}$$

and the total phase difference for the thickness t is

$$\Delta = \Delta_0 t = t\sqrt{\delta_0^2 + (2\rho_0)^2}. \tag{3}$$

If the incident light is polarised with its plane parallel to one of the two principal vibration directions, then ψ is given by the relation (Pockels)

$$\tan 2\psi = \frac{\sin 2\gamma \sin \Delta}{\cos^2 2\gamma + \sin^2 2\gamma \cos \Delta}. \tag{4}$$

The total rotation for the solid when there is no birefringence is $\rho = t\rho_0$ and the total phase retardation when there is no rotation is $\delta = t\delta_0$.

From (1) and (2) we have

$$\sin 2\gamma = 2\rho_0/\Delta_0 = 1/m \text{ (say)} \tag{5}$$

or

$$\Delta = 2m\rho \tag{6}$$

Equation (4) could be written as

$$\tan 2\psi = \frac{\sin 2\gamma \sin \Delta}{1 - \sin^2 2\gamma (\cos \Delta - 1)}. \tag{7}$$

Substituting (5) and (6) in (7) and expanding sin $2m\rho$ and cos $2m\rho$ we have

$$\tan 2\psi = 2\rho \left[1 - \frac{m^2(2\rho)^2}{3!} + \frac{m^4(2\rho)^4}{5!} - \frac{m^6(2\rho)^6}{7!} \cdots\right]$$

$$\times \left[1 + \frac{(2\rho)^2}{2!} - \frac{m^2(2\rho)^4}{4!} + \frac{2\rho^4}{[2!]^2} + \frac{2\rho^6}{[2!]^3} \cdots\right] = \mathrm{L}$$

$$\therefore \quad 2\psi = \tan^{-1}\mathrm{L} = \mathrm{L} - \frac{\mathrm{L}^3}{3} + \frac{\mathrm{L}^5}{5} \cdots$$

substituting the values of L we have

$$2\psi = 2\rho \left[1 - \frac{m^2 - 1}{3!}(2\rho)^2 + \frac{(m^2 - 1)(m^2 + 6)}{5!}(2\rho)^4 \cdots\right]$$

but $(m^2 - 1)(2\rho)^2 = \delta^2$

$$\therefore \quad 2\psi = 2\rho \left(1 - \frac{\delta^2}{3!} + \frac{(m^2 + 6)}{5!}(2\rho)^2\delta^2 \cdots\right) \tag{8 a}$$

This series is convergent when ρ is not very large and δ is less than one. When δ is very small

$$2\psi = 2\rho\,(1 - \delta^2/3!). \tag{8}$$

This formula can be very easily verified by experiment using the usual Faraday effect apparatus with the half-shade mounted at the analyser end. The magnetic rotation ρ in an isotropic rectangular block of glass is measured for a known value of the magnetic field. The glass is then strained by applying pressure. The plane of polarisation of the incident light is made parallel to the axis of strain. The birefringence introduced (δ) is measured with the aid of a Babinet compensator and finally the value of ψ for the strained glass is measured for the same value of the magnetic field. In practice ρ and ψ are taken as the mean of the rotations obtained for positive and negative magnetic fields.

Fig. 1 gives the theoretical curve together with the experimental points. The agreement between theory and experiment is satisfactory. It is to be

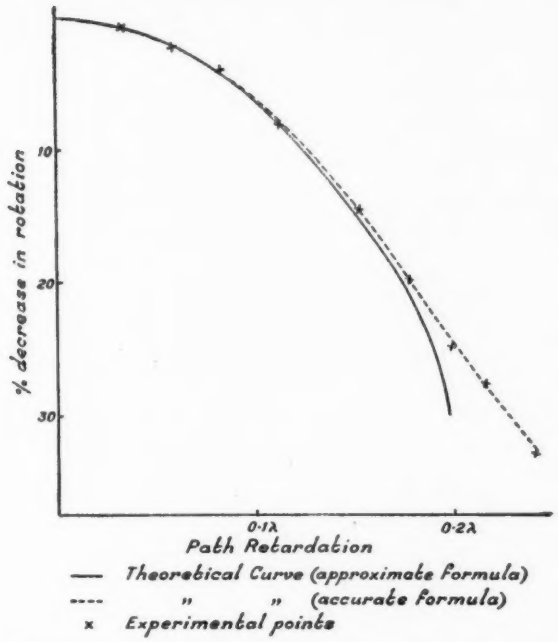

FIG. 1. Variation of rotation with birefringence (for small values of birefringence)

noticed that even when δ is nearly $\lambda/6$, the deviation from the approximate formula is not more than 3%. If the second term in expression (8 *a*) is also taken, a greater accuracy is obtained.

The formula (8) is approximately true for both inherent and accidental birefringence. Since the decrease in the rotation is proportional to $\delta^2/3$!, small birefringences of the order of $\lambda/30$ do not affect the results by more than 1%. This is quite obvious from Fig. 1. Further the decrease is dependent on the *total phase retardation* ($\delta = t\delta_0$) and not on δ_0 alone, and the Faraday rotation is not affected by the presence of birefringence if $\delta = t\delta_0 \simeq 0$. This can be achieved by two methods. The first is to have $\delta_0 = 0$, *i.e.*, to choose crystals that show no traces of birefringence. The second is to make the thickness t small, even though $\delta_0 \neq 0$ so that $t\delta_0$ is very nearly zero. Obviously if the birefringence δ_0 is large, the thickness t must be very small. This would necessitate the use of very accurate methods of measurements since the magnitude of the rotation would also be correspondingly reduced. But it is advantageous to reduce the thickness provided such accurate methods are available, because the *percentage* error introduced by the birefringence is

appreciably reduced thereby. Indeed by using larger thicknesses it may be possible to increase the inherent accuracy of the measurement of 2ψ, but it would differ from the true value 2ρ by a sensible amount due to the *accidental* birefringence that is present (the magnitude of which cannot be readily estimated).

These inferences from theory find direct confirmation in the measurements made on diamond and alumina (Ramaseshan, 1946). As is well known, although birefringence is not an inherent property of diamond, most diamonds exhibit accidental birefringence. It was invariably found that the values of Verdet constant obtained with thin specimens were always higher and more consistent than those obtained with thicker specimens.

3. Birefringence Large Compared to Rotation

A second formula can be derived in the case when ρ_0 the rotation is much smaller than δ_0 the birefringence. Equation (4) of the last section may be written as

$$\tan 2\psi = \frac{\sin 2\gamma \sin \Delta}{1 - 2 \sin^2 2\gamma \sin^2 \Delta/2}$$

putting $\sin 2\gamma = 2\rho_0/\Delta_0 = \epsilon$ and expanding we get

$$\tan 2\psi = \epsilon \sin \Delta (1 + 2\epsilon^2 \sin^2 \Delta/2 + 4\epsilon^4 \sin^4 \Delta/2 \ldots)$$

and when $2\rho_0/\delta_0$ is small

$$\tan 2\psi = \epsilon \sin \Delta = \frac{2\rho_0}{\Delta_0} \sin \Delta$$

or

$$\tan 2\psi = \frac{2\rho}{\Delta} \sin \Delta. \tag{9}$$

While the formula in the previous section could only be used when the total phase difference is small, the formula (9) can be used for all values of birefringence provided the ratio $2\rho_0/\delta_0$ is small. One notices that ψ is an oscillating function and is zero when $\Delta = 0$ and $\Delta = \pi$ and has a positive maximum at $\Delta \simeq \pi/2$ and a negative one at $\Delta \simeq 3\pi/2$. The maximum value that ψ can take is when

$$\cos \Delta = -\tan^2 2\gamma$$

and

$$\psi_{max.} = \tfrac{1}{2} \text{ arc sin } \frac{2\rho_0}{\delta_0} \tag{10}$$

The equation (9) has been verified by experiments on strained plastic plates. Most transparent colourless plastic sheets that are sold in the market

exhibit permanent strains probably due to the calendering during manufacture and behave like uniaxial crystals with very small birefringence. The direction of the optic axis is perpendicular to the large extensive surface of the plate. From such a plate, a large number of pieces were cut with lengths varying from 0·5 cm. to 8 cm. The sides were polished and due care was taken to see that no undue strains were introduced during the cutting and polishing processes. The rotatory power ρ_0 in the absence of birefringence was obtained by measuring the rotation along the optic axis. Each plastic piece was then placed with its optic axis perpendicular to the magnetic field and its birefringence in the absence of the field was measured with the aid of a Babinet compensator. It was found that the path retardation was proportional to the thickness of the piece. The incident light (which is an accurately parallel beam) had its plane of vibration parallel to one of the principal vibration directions of the plastic piece. The value of ψ was determined by means of a half-shade at the analyser end, it being taken as the mean of values obtained when the magnetic field was put on and reversed. The same field was used for all the specimens.

Tables I and II give the results of the experiment for the two wavelengths λ 5461 and λ 4358 and Fig. 2 represents the variation of ψ with the thickness of the specimens for λ 5461 and λ 4358. In the plastics as $2\rho_0/\delta_0$ is constant and as $2\rho_0 \ll \delta_0$, Δ can be taken to be equal to δ. Therefore from (9 *a*) tan ψ is proportional to sin Δ which is exactly what the curves in Fig. 2 depict.

TABLE I

Magnetic rotation in strained plastic plates for λ 5461

Magnetic field = 4050 Oersteds ρ_0 = 60 minutes

Thickness	Phase difference $X\pi$	Rotation 2ψ		$\frac{V^*}{V}$
		Calculated	Observed	
0·54	0·12	31′	21′	0·68
1·21	0·34	63′	55′	0·79
1·70	0·40	79′	73′	0·75
2·26	0·50	84′	80′	0·61
3·05	0·70	71′	70′	0·40
3·51	0·80	51′	48′	0·24
4·10	0·95	18′	22′	0·10
4·78	1·10	−23′	−18′	−0·06
5·60	1·30	−62′	−55′	−0·17
6·50	1·50	−83′	−82′	−0·22
7·19	1·60	−77′	−68′	−0·17

TABLE II

Magneto-optic rotation in strained plastic plates for λ 4358

Magnetic field = 4050 Oersteds $\rho_0 = 101{\cdot}2$ minutes

Thickness	Phase difference $X\pi$	Rotation 2ϕ		$\frac{V^*}{V}$
		Calculated	Observed	
0·54	0·15	53′	41′	0·76
1·21	0·36	94′	85	0·71
1·70	0·50	108.	102′	0·61
2·26	0·66	100′	96′	0·42
3·05	0·85	50′	54	0·18
3·51	1·00	0′	8′	0·12
3·10	1·15	− 47′	− 52′	−0·13
4·78	1·35	− 95′	− 90′	−0·09
5·60	1·60	−104′	−100′	0·18
6·50	1·85	− 55′	− 60′	−0·09
7·10	2·00	0′	8′	−0·00

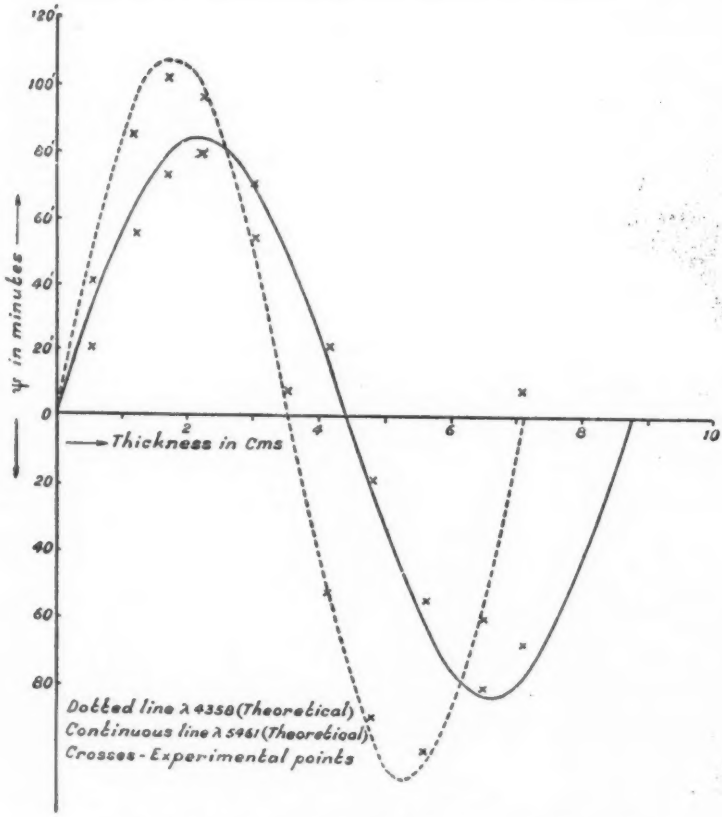

FIG. 2. The variation of ϕ with thickness in strained plastics

From the curves one notices that for small values of thickness, the rotation is proportional to t, *i.e.*, the magnitude of the rotation is not affected when the birefringence is small. Another point of interest is that for values of thickness between 3·5 and 4·5 cm., ψ for λ 5461 is positive while that for λ 4358 is negative. The maximum value of the rotation is found to obey formula (10) within about 3%.

The apparent Verdet constant V* can be defined as

$$V^* = \frac{\psi}{Ht}$$

where H is the magnetic field. If ψ is small

$$\frac{V^*}{V} = \frac{\psi}{R} = \frac{\sin \Delta}{\Delta}$$

The experimental value of V*/V are given in the last column of Tables I and II. Fig. 3 represents the theoretical curve showing the variation of V*/V

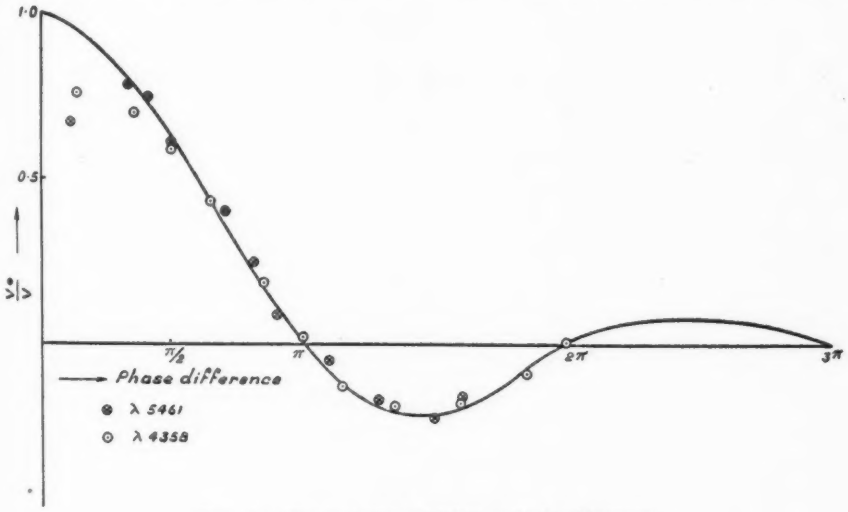

FIG. 3. The variation of V*/V with birefringence

with birefringence together with the experimental points. The agreement between theory and experiment is quite satisfactory. It may be mentioned that the magnetic rotations observed in most solids are not very great and the formulæ (8) and (9) together cover practically all the cases that are likely to occur in experimental observations of magneto-optic rotation in strained solids.

4. Measurement of Birefringence by the Magneto-Optic Method

From Fig. 3 one notices that the value of the magnetic rotation decreases as the birefringence increases. The decrease is first slow till the birefringence has a value of $\lambda/8$. From $\lambda/8$ to $\lambda/2$ the decrease in rotation is almost proportional to the increase in the birefringence. The decrease in the magnetic rotation can, therefore, be used as a fairly sensitive method for the measurement of the birefringence in a solid and the sensitivity is greatest when the value of the birefringence is between $\lambda/8$ and $\lambda/2$. This method has been used to measure the photoelastic constants in some glasses and crystals, the results of which will be reported in a later paper.

The authors' thanks are due to Prof. R. S. Krishnan for the kind interest he took in this investigation and to Dr. G. N. Ramachandran and Mr. V. Chandrasekharan for the discussions and helpful suggestions they gave during the course of these researches.

Summary

Approximate formulæ correlating the decrease in Faraday rotation with birefringence have been derived and these have been verified by experiments on strained glasses and plastics. It is found that for small values of birefringence, the decrease in the Faraday rotation is proportional to the square of the total birefringence. For values of the birefringence of $\lambda/30$, the decrease in the rotation is less than 1%. The Verdet constant in birefringent solids can be accurately determined provided sufficiently thin specimens are taken such that the total birefringence is small. Finally it is shown that the decrease in the Faraday rotation can itself be used as an accurate measure of the birefringence in strained solids.

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ON THE POLYNOMIAL $\pi_n(x)$

By K. P. Bhatnagar

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The polynomial $\pi_n(x)$, suggested by A. Angelescu,[1] is defined by[2]

$$\pi_n(x) = e^x \frac{d^n}{dx^n}\left[e^{-x} A_n(x)\right]$$

where

$$A_n(x) = (a_0, a_1, a_2, \ldots\ldots a_n, x, 1)^n.$$

It is possible to express the polynomial $\pi_n(x)$ in terms of moment constants μ_r defined by

$$\mu_r = \int_0^\infty t^r d\beta(t), \qquad r = 1, 2, 3\ldots\ldots$$

To show this, we first note that $\frac{A_n(x)}{n!}$ is an Appell set, *i.e.*,

$$\frac{d}{dx}\left[\frac{A_n(x)}{n!}\right] = \frac{A_{n-1}(x)}{(n-1)!}$$

We now use Sheffer's result,[3] *viz.*, that an Appell polynomial, say $B_n(x)$ is given by

$$B_n(x) = \int_0^\infty \frac{(x+t)^n}{n!} d\beta(t)$$

This gives

$$\frac{\pi_n(x)}{n!} = e^x \frac{d^n}{dx^n}\left[\frac{e^{-x}}{n!}\int_0^\infty \sum_{r=0}^{n} n c_r x^{n-r} t^r d\beta(t)\right.$$

$$= \frac{e^x}{n!}\sum_{r=0}^{n} n c_r \mu_r \frac{d^n}{dx_n}\left[e^{-x}x^{n-r}\right]$$

$$= \sum_{r=0}^{n} (-1)^r n c_r \mu_r \frac{(n-r)!}{n!} L_{n-r}^r(x).$$

where $L_n^r(x)$ denotes generalised Laguerre polynomial.

Hence $$\pi_n(x) = \sum_{r=0}^{n} \frac{(-1)^r n!\, \mu_r}{r!} L_{n-r}^r(x).$$

I am grateful to Dr. R. S. Varma for suggesting this problem and for his guidance in its preparation. I am also grateful to the U.P. Government for the award of a Research Assistantship which has enabled me to carry out these investigations and to the University of Lucknow for providing research facilities.

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CHEMOTHERAPY OF MALARIA

III. Attempted Synthesis of Biguanide and Guanidino Derivatives of Quinoline

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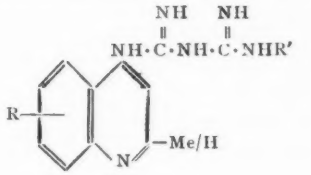
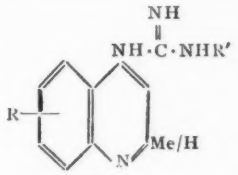
Received April 24, 1951

The main object of this work is to discover compounds that would show intensive action against both the erythrocytic and exoerythrocytic forms of plasmodia so that such compounds could be expected to be cures against vivax malaria. The 4-aminoquinoline derivatives so far tried do show very intensive action against the erythrocytic forms and, in addition, possess many desirable properties from the clinical point of view, such as a slow rate of excretion, quick action and absence of toxic effects in therapeutic doses. But these quinoline derivatives tried so far do not show any activity against the exoerythrocytic forms so that this has even led some workers to rationalise that the 4-aminoquinolines can be expected to possess activity against the erythrocytic forms of the plasmodia only. Since some 4-hydroxyquinolines have recently been reported to show activity against the exoerythrocytic forms,[1] we cannot rule out the possibility that some 4-aminoquinolines may also show this activity, only it may be a question of finding out the right type of substituents and side chains attached to the quinoline nucleus. With this hypothesis in view, we have been engaged in the synthesis of quinolines possessing groups present in compounds that show activity



(I)

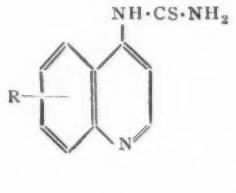


(II)

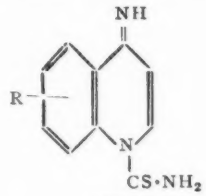
against the exoerythrocytic forms. This paper relates to the attempts to synthesise the quinolines of types (I) and (II). Though compounds of the above types could not be synthesised, the work carried out revealed some interesting properties of the 4-aminoquinolines which were used as the starting materials.

Though a large number of 4-substituted aminoquinoline derivatives have been synthesised, the aminoquinolines themselves have not received equal amount of attention.[2] The 4-aminoquinolines have been prepared from the corresponding carboxylic acids by the Hofmann or Curtius reaction in yields of about 60 to 75%.[3] But this method is limited in application because the 4-carboxylic acids are not always easily accessible. Other methods which have been tried are: amination with potassium amide,[4] reduction of hydrazino derivatives with red phosphorus and hydroiodic acid,[5] treatment of the methoxy or phenoxy derivatives with ammonium acetate[6] and the treatment of corresponding sulphite derivative with ammonia under pressure.[7] The simple method of converting the easily prepared 4-chloroquinolines with ammonia was reported after the work was started. While the treatment of 4-chloroquinoline with aqueous ammonia or ammonia under pressure gave only bad yields of the aminoquinoline, good yields are obtained by passing ammonia gas through a hot mixture of the chloroquinoline and phenol.[8] We have studied this method in detail and have found that this reaction proceeds best at a temperature of about 130° to 140° C. We have accordingly prepared 4-amino-7-chloroquinoline, 4-amino-6-methoxyquinaldine, 4-amino-8-methoxyquinaldine and 4-amino-6-chloroquinaldine.

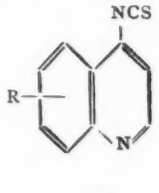
We attempted the synthesis of guanidino and biguanide derivatives of types (I) and (II) starting from the thiocarbamidoquinoline (III) as yet unknown, according to the standard methods available.[9] But the attempts to prepare this thiocarbamido derivative ended in failure. Treatment of 4-amino-7-chloroquinoline with thiocyanic acid even in great excess, led to the formation of a crystalline product which because of correct analytical



(III)



(IV)



(V)

figures was first mistaken to be the required thiourea derivative (III). But the treatment of this with desulphurising agents, methyl iodide, chloracetal, etc., gave back only 4-amino-7-chloroquinoline. Further experiments showed that even the possible alternative formula (IV) had to be ruled out for this compound and it was found to be only the thiocyanic acid salt of 4-amino-7-chloroquinoline. The next attempt to prepare the same thiourea derivative

through the isothiocyanate derivative (V) also ended in a failure because this compound (V) itself could not be prepared. Treatment of 4-amino-7-chloroquinoline with carbon disulphide and ammonia yielded a product which appeared to be the dithiocarbamate derivative but this could not be desulphurised.

In view of the peculiar behaviour of the amino group, the reactions of this compound were further studied. Excepting acetylation with acetic anhydride whereby it yielded an acetyl derivative, no other reaction characteristic of the aliphatic or aromatic amines could be carried out. 4-Amino-7-chloroquinoline did not react with acetsulphanilylchloride (differing from 4-aminopyridine) or *p*-chlorophenyl isothiocyanate or isopropylisothiocyanate.[10] It remained unchanged on treating with S-methylisothiourea sulphate, *p*-chlorophenylcyanamide, dicyandiamide or isopersulphocyaric acid. Treatment with nitrous acid did not lead to diazotisation though from the reaction product a small quantity of 4-hydroxyquinoline could be isolated. Thus the quinoline ring has modified the properties of the amino group to such an extent that it exhibits the properties of neither the aliphatic nor the aromatic amino group. This is evidently because of resonance noticed in the aminoquinolines[11] and it is interesting to find out whether the striking antimalarial activity met with in these 4-aminoquinolines is due to this physical or chemical property.

4: 7-Dichloroquinoline could not be converted into the 4-guanidino derivative (II) by treatment with guanidine salts under different conditions. Same was the result when 4-alkoxy-7-chloroquinoline was used in the place of 4: 7-dichloroquinoline.

Experimental

4-Aminoquinoline and Derivatives.—A number of experiments were tried to prepare this compound from 4: 7-dichloroquinoline by the action of ammonia. The dichloroquinoline heated with alcoholic ammonia (8%) at 100° for 4 hours in an autoclave (75 lb. pressure), or at 150–60° (250 lb. pressure) did not furnish the amino compound. The aminoquinoline was prepared by a method also followed by Elderfield, *et al.*[8] but the yields in our hands were about 95% while Elderfield, *et al.*, have reported only 52%.

4: 7-Dichloroquinoline (60 g.) was dissolved in freshly distilled phenol (300 g.) and dry ammonia gas was passed into the mixture maintained at 130–40° for 3 hrs. The contents were then cooled, treated with sodium hydroxide solution (3 l. of 10%), the precipitate obtained after cooling in the ice-bath for 2 hrs. was filtered off, washed with cold water and dried. The crude gray amino compound was dissolved in acetone and dry hydrogen

chloride passed into it whereby the hydrochloride of 4-amino-7-chloroquinoline separated. Yield, 62 g., m.p. 284–86°.

The free base was obtained from the hydrochloride by basification. On being crystallised from dilute alcohol, it melted first at 105–10°, resolidified and melted again at 148–50° C. However, when crystallised from benzene, the product had m.p. 150–51°. The latter is the anhydrous product while the former is the hydrate. Picrate, m.p. 295–7° C. Acetyl derivative, obtained in needles from alcohol, had m.p. 195° (Found: N, 12·57. $C_{11}H_9ON_2Cl$ requires N, 12·72%).

Treatment of the aminoquinoline hydrochloride with potassium or ammonium thiocyanate, or the base with excess of thiocyanic acid furnished a product, m.p. 201–2° (Found: N, 17·85. $C_9H_7N_2Cl$, HCNS requires N, 17·58%) which was identified to be the thiocyanic acid salt. This compound on treatment with ammonium hydroxide furnished the free aminoquinoline, while the filtrate gave the characteristic blood coloration with ferric chloride indicating the presence of the thiocyanate ion. The thiocyanic acid salt on treatment with picric acid furnished the picrate of 4-amino-7-chloroquinoline, m.p. 295–7°.

4-*Amino*-6-*methoxyquinaldine*.—4-Chloro-6-methoxyquinaldine (60 g.) was dissolved in phenol (300 g.) and dry ammonia gas was passed into the mixture maintained at 150–60° for 3·5 hrs. The reaction mass was worked up as before and the aminoquinaldine isolated as the hydrochloride (68% yield). The base generated from it crystallised from ethanol in flakes, m.p. 207–8° (Found: N, 15·04. $C_{11}H_{12}ON_2$ requires N, 14·89%). The hydrochloride separated in prisms from alcohol and had m.p. 262–3° (Found: N, 12·00. $C_{11}H_{12}ON_2$, HCl requires N, 12·47%). Picrate, m.p. 245–6°. The sulphate, more soluble than the hydrochloride had m.p. 233–34°. The acetyl derivative prepared by the action of acetic anhydride, had m.p. 230° (Found: N, 11·71. $C_{13}H_{14}O_2N_2$ requires N, 12·17%). The thiocyanate prepared by the action of potassium thiocyanate on the hydrochloride crystallised from alcohol and had m.p. 220–22° (Found: N, 16·88. $C_{11}H_{12}ON_2$, HCNS requires N, 17·0).

4-*Amino*-6-*chloroquinaldine*.—This was prepared in 96% yield by the action of ammonia on 4:6-dichloroquinaldine in phenol. The base had m.p. 188–89°. The hydrochloride crystallised from alcohol in needles and had m.p. 272–73° (Found: N, 10·78. $C_{10}H_9N_2Cl$, 2 HCl requires N, 10·55%). Picrate, needles from alcohol, m.p. 262–64°. Thiocyanate, m.p. 212–4°. (Found: N, 16·99. $C_{10}H_9N_2Cl$, HCNS requires N, 16·7%.)

The acetyl derivative had m.p. 226–7° (Found: N, 11·8. $C_{12}H_{11}ON_2Cl$ requires N, 11·94%).

4-*Amino*-8-*methoxyquinaldine*.—4-Chloro-8-methoxyquinaldine (10 g.) in freshly distilled phenol (50 g.) was treated with ammonia gas for 3·5 hrs. at 130–40° and the product worked up as usual. The free amine (yield 4·6 g.) obtained on crystallisation from acetone had m.p. 229–30°. The hydrochloride had m.p. 259–60° (Found: N, 10·30. $C_{11}H_{12}ON_2$, 2 HCl requires N, 10·73%). Picrate, m.p. 252–4°.

6-*Chloro*-8-*aminoquinoline*.—Reduction of the nitroquinoline with Raney nickel catalyst and hydrogen proved to be a very convenient method. 6-Chloro-8-nitroquinoline (10 g.) dissolved in alcohol (100 c.c.) was subjected to reduction with hydrogen in Raney nickel at 50 lb. at 30° C. The amino quinoline was obtained in quantitative yield (8·43 g.), m.p. 72–4°; hydrochloride, m.p. 216–8°; picrate, m.p. 252–54°. Acetyl derivative, m.p. 147–8°.

Ammonium 7-*chloroquinoline*-4-*dithiocarbamate*.—To a mixture of 4-amino-7-chloroquinoline (5·5 g.), ethanol (10 c.c.) and liquor ammonia (8 c.c.), carbon disulphide (5 c.c.) was added dropwise with good shaking. The mixture warmed up when a clear solution was obtained which on cooling deposited a crystalline product which was collected. On crystallisation from water it separated in needles, m.p. 148° (Dec.) (Found: N, 15·50; Cl, 12·79. $C_{10}H_{10}N_3S_2Cl$ requires N, 15·47; Cl. 13·07%).

This compound could not be desulphurised to the corresponding isothiocyanate.

Summary

Of the methods available for the synthesis of the 4-aminoquinoline derivatives, the best one was found to consist of passing ammonia into a mixture of 4-chloroquinolines and phenol maintained at 130–60°. Accordingly 4-amino-7-chloroquinoline, 4-amino-6-methoxyquinaldine, 4-amino--8-methoxy quinaldine, and 4-amino-6-chloroquinaldine were prepared in good yields. Attempts to prepare the guanidine and biguanide derivatives of formula (I) and (II) failed. The amino group in position 4 of the quinolines showed properties of neither the aliphatic nor the aromatic amino group.

4-Chloroquinolines do not react with guanidine salts to yield the 4-guanidinoquinolines. Similarly 4-methoxyquinolines also do not react with guanidine salts.

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RUBIN NUMBER OF SOME HYDROXY COMPOUNDS

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Introduction

'Gold Number'[1] gives a measure of the protective action of a hydrophilic colloid. Hence a determination of gold number of sugars and sugar products gives a measure of the hydrophilic colloids present in them. In view of the difficulties in preparing the gold sol, rubin number can be used with advantage in the place of gold number. A measure of the rubin number of sugars has been made in the case of pure sucrose and a few white consumption sugars.[2] Although "Analar" sucrose is not a protective colloid by itself nor can have any appreciable quantity of protective colloids as impurities, it is found that it has a protective action on congo rubin. That this may be due to a possible interaction between sucrose and rubin is seen from the absorption characteristics of the mixture.[2] Hence it is of interest to study the behaviour of rubin with other substances of similar structure. This paper deals with the rubin number of some hydroxy compounds. The rubin number is determined by adopting the new technique developed by Doss and Kalyanasundaram.[3]

Experimental

(1) *Materials used.*—(i) Congo rubin: Congo rubin of purity 99·5% is obtained by purifying the Kahlbaum product by the method employed by Doss[4] for benzopurpurin 10 B. The purity has been determined by finding out the percentage of sulphated ash.

(ii) The buffer solution of pH 5·1 is prepared from sodium acetate and acetic acid, the pH being determined by the quinhydrone electrode.

(iii) Galactose and ethyl alcohol are pure products of Merck whereas maltose, and glycerine are of B.D.H. (Laboratory Reagent) quality. Lactose is of Kahlbaum quality. Glucose is B.P. quality supplied by the Corn Products Refining Company.

(2) *Procedure.*—5 c.c. of 0·004% aqueous solution of Congo rubin is mixed with 0·5 c.c. of the buffer of pH 5·1 and the required quantity of the substance under examination. The mixture is made up to 10 c.c. and

allowed to stand for 3 minutes. 1 c.c. of 10% sodium chloride in water is then added and the mixture heated to a temperature of 60° C. for 10 minutes and cooled to room temperature. The solution is then centrifuged to remove the blue dye in suspension. The red colour of the centrifugate is then measured by the Spekker absorptiometer using No. 604 green filter and a 0·5″ cell. The observed Spekker readings are corrected for the colour due to the substance present.

The rubin number is defined as the number of milligrams of substance necessary for obtaining a residual colour of $\frac{22{\cdot}0 + 97{\cdot}9}{2} = 60$ units of Spekker reading. The results are given in Tables I to VI and Fig. 1.

TABLE I. *Lactose*

Mg. of substance in 10 c.c. of solution	Colour of centrifugate: Spekker reading	Spekker reading for substance present	Corrected Spekker reading
0	22·0	..	22·0
100	23·3	0	23·3
200	24·2	0	24·2
300	25·4	0·1	25·3
400	25·2	0·1	25·1
800	28·2	0·2	28·0
1000	30·3	0·3	30·0
1500	37·6	0·4	37·2
2000	41·3	0·6	40·7
2500	58·8	0·7	58·1
3000	97·8	0·8	97·0
Colloid and no salt	97·9	..	97·9

TABLE II. *Maltose*

Mg. of substance in 10 c.c. of solution	Colour of centrifugate: Spekker reading	Spekker reading for substance present	Corrected Spekker reading
0	22·0	..	22·0
200	23·5	0	23·5
400	25·2	0·1	25·1
800	28·0	0·2	27·8
1000	30·8	0·3	30·5
2000	41·4	0·5	40·9
3000	55·6	0·8	54·8
4000	77·8	1·0	76·8
5000	100	1·3	98·7
Colloid and no salt	97·9	..	97·9

TABLE III. *Galactose*

Mg. of substance in 10 c.c. of solution	Colour of centrifugate: Spekker reading	Spekker reading for substance present	Corrected Spekker reading
0	22·0	..	22·0
400	23·4	0·1	23·3
800	25·3	0·2	25·1
2000	32·5	0·5	32·0
2500	35·6	0·7	34·9
3000	42·4	0·8	41·6
4000	56·2	1·0	55·2
5000	97·0	1·3	95·7
Colloid and no salt	97·9	..	97·9

TABLE IV. *Glucose*

Mg. of substance in 10 c.c. of solution	Colour of centrifugate: Spekker reading	Spekker reading for substance present	Corrected Spekker reading
0	22·0	.	22·0
1000	25·2	0·2	25·0
2000	27·7	0·5	27·2
3000	32·0	0·8	31·2
4000	35·2	1·0	34·2
5000	42·2	1·3	40·9
6000	55·2	1·6	53·6
7000	66·8	1·9	64·9
Colloid and no salt	97·9	..	97·9

TABLE V. *Glycerine*

Mg. of substance in 10 c.c. of solution	Colour of centrifugate: Spekker reading	Spekker reading for substance present	Corrected Spekker reading
0	22·0	..	22·0
609	29·2	0·1	29·1
1217	30·5	0·1	30·4
1460	39·3	0·1	39·2
1704	44·6	0·1	44·5
2191	55·2	0·1	55·1
2434	65·0	0·1	64·9
3651	99·8	0·2	99·6
Colloid and no salt	97·9	..	97·9

TABLE VI. *Ethyl Alcohol*

Mg. of substance in 10 c.c. of solution	Colour of centrifugate: Spekker reading	Spekker reading for substance present	Corrected Spekker reading
0	22·0	..	22·0
399	25·4	..	25·4
639	29·8	..	29·8
798	29·8	..	29·8
1038	45·3	..	45·3
1197	49·0	..	49·0
1437	96·2	..	96·2
1596	100	..	100
Colloid and no salt	97·9	..	97·9

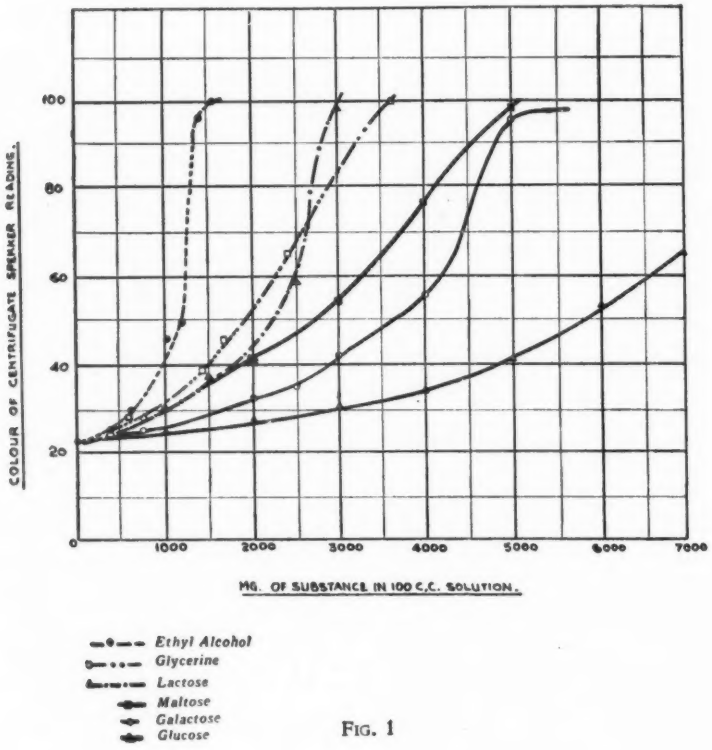

FIG. 1

TABLE VII

Substance	Rubin Number	Rubin Number expressed in Millimols.
Lactose ..	2550	7·46
Maltose ..	3280	9·59
Sucrose* ..	3100	9·07
Galactose ..	4200	23·3
Glycerine ..	2310	25·1
Ethyl Alcohol ..	1210	26·3
Glucose ..	6500	36·1

* Doss and Kalyanasundaram.[2]

DISCUSSION

It is found that the rubin numbers (Table VII) vary considerably with the different compounds examined, it being a minimum with ethyl alcohol and maximum with glucose. A fundamental comparison is somewhat difficult as the rubin number is expressed in milligrams. A more useful procedure would be to express the rubin number in millimols. The values thus obtained are given in column 3 of Table VII. An examination of these values reveals that the disaccharides have a low rubin number whereas the monosaccharides and the alcohols have a rubin number in the neighbourhood of 25. The low values obtained in the case of disaccharides is not simply due to their molecular weights being double that of hexoses. It appears when two hexoses join to form the disaccharide, the protection action of the combination is better than what should be expected on the basis of additivity. It will be of interest from this point of view to investigate the rubin number of other sugars and allied hydroxy compounds.

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SUMMARY

The rubin number of some hydroxy compounds has been determined. It is found that the disaccharides have a better protective action on congo rubin than the monosaccharides.

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CHEMOTHERAPY OF MALARIA

IV. Synthesis of 4-(Guanidylphenylamino)quinolines

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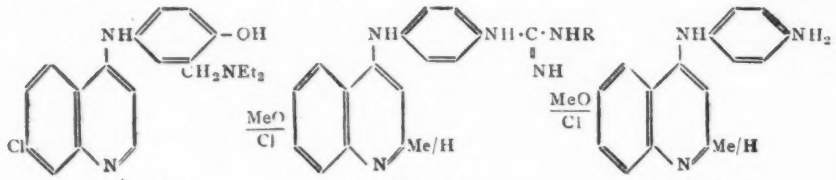
Of the hundreds of 4-aminoquinolines tried against malaria, two classes of compounds have been found to show good therapeutic action: (1) those having an aliphatic side chain terminating in an alkylamino group, such as chloroquin or oxychloroquin, and (2) those having a benzene ring bearing further basic substituents, such as "camoquin" (I). The compounds of second group are easier to synthesise and also manufacture, but the possibilities in this direction have not been fully explored. The attempts to synthesise quinoline derivatives with a guanidine or biguanide side chain at the position 4 having proved a failure as shown in the previous part, as the next best, the synthesis of 4-phenylaminoquinoline derivatives with a guanidine radical substituted in the benzene ring (II) was taken up. This paper records the attempts made to work out a general method of synthesis of compounds of type (II) which could be used to synthesise a variety of quinolines.



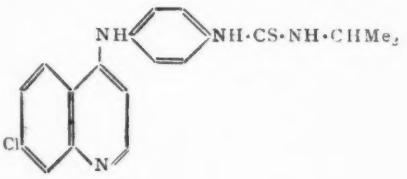
(I) (II) (III)

Since we wanted to introduce a variety of substituents (R) in the guanidine residue, attempts were made to synthesise the guanidine derivatives starting from the compound (III). By reacting 4-chloro-6-methoxyquinaldine with *p*-phenylenediamine at 130–40°, Slater[1] obtained 4-(*p*-aminoanilino)-6-methoxyquinaldine, which on acetylation furnished the corresponding acetamino compound. These two compounds have now been prepared by treating 4-chloro-6-methoxy quinaldine with acetphenylenediamine and then hydrolysing the resulting acetamino compound. Similarly, by using 4-chloro-8-methoxy-quinaldine, 4:6-dichloroquinaldine and

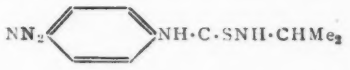
4:7-dichloroquinoline and treating them individually with *p*- acetphenylenediamine, we obtained respectively 4-(*p*-acetaminoanilino)-8-methoxyquinaldine, 4-(*p*-acetaminoanilino)-6-chloroquinaldine and 4-(*p*-acetaminoanilino)-7-chloroquinoline. These on hydrolysis furnished the corresponding free-amino compounds. *p*-Nitraniline condensed with 4:7-dichloroquinoline to furnish 4-(*p*-nitroanilino)-7-chloroquinoline which on reduction with iron and acetic acid furnished the corresponding amino compound prepared as indicated above. *p*-Bromoaniline was found to condense easily with 4:7-dichloroquinoline. In all these reactions, the chlorine atom in position 4 of the quinoline ring very readily reacted with the aromatic amino group irrespective of the nature of the substituent in the benzene ring. The facility of this reaction in the present case is in sharp contrast to those reported in the previous part when we attempted to condense the chloroquinolines with guanidines.

The conversion of the aminoanilinoquinolines (II) into the corresponding guanidine derivatives (II) could be achieved by (i) treatment with the appropriate S-methylisothiourea derivative, (ii) reacting with the suitable cyanamide derivative and (iii) by desulphurising the corresponding thiourea derivative in the presence of alcoholic ammonia. Since the thiourea derivatives are easy to prepare, the last method was then tried.

4-(*p*-Aminoanilino)-7-chloroquinoline reacted with isopropylisothiocyanate to furnish the corresponding thiourea derivative, 4-(*p*-isopropylthiocarbamidoanilino)-7-chloroquinoline (IV). The structure of this compound has been confirmed by the fact that it could be obtained by the action of *p*-aminophenylisopropylthiourea (V) on 4:7-dichloroquinoline. It should be noted that in this reaction, the chlorine atom in position 4 of the



(IV)



(V)

quinoline ring reacts with the aromatic amino group and the chloroquinoline does not behave like an alkylhalide in which case an S-quinolyl derivative would be expected. The thiourea derivative (IV) on treatment with mercuric oxide and alcoholic ammonia did undergo desulphurisation very readily even in cold, but instead of yielding the guanidine of the type (II), the cleavage of the side chain appears to take place. The compound obtained

which is free from sulphur but contains chlorine, could not be identified so far; it is neither the 4-amino-7-chloroquinoline nor 4-hydroxy-7-chloroquinoline.

Being impressed with the ease with which the chlorine atom in position 4 of the quinoline ring reacts with aromatic amino group, the synthesis of the required guanidine derivative (II) was attempted by reacting 4:7-dichloroquinoline with 4-aminophenylguanidine. This reaction proceeds on easily and the required guanidine derivative was obtained; though this compound crystallised nicely, it did not give very good analytical figures for nitrogen in the micro Duma's method. That the guanidine group of *p*-aminophenylguanidine does not participate in this reaction has been checked by allowing 4:7-dichloroquinoline to react with *p*-tolylguanidine and isopropylguanidine individually under identical conditions which did not furnish the condensation products. 4:7-Dichloro-quinoline condensed with *p*-aminophenylisopropylguanidine to furnish the corresponding guanidine derivative of formula (II). This reaction appears to be the best for the preparation of compounds of formula (II) and is being extended to synthesise a number of derivatives.

Experimental

4-(p-*Acetaminoanilino*)-7-*chloroquinoline*.—An intimate mixture of 4:7-dichloroquinoline (3 g.), *p*-aminoacetanilide (2·06 g.) and phenol (15 g.) was heated in an oil-bath at 150-60° for 4 hrs. The reaction mixture was cooled and poured into 10% sodium hydroxide solution. After allowing to stand for 2 hrs., the product was filtered, washed with water (yield of crude compound, 4·65 g.) and repeatedly crystallised from ethanol from which it separated in microscopic needles, not melting below 290° (Found: N, 13·62. $C_{17}H_{14}ON_2Cl$ requires N, 13·48%). The same product could be prepared by refluxing the constituents in alcohol for 1·5 hrs.

4-(p-*Aminoanilino*)-7-*chloroquinoline*.—The foregoing compound (5 g.) was suspended in con. hydrochloric acid (20 c.c.) diluted with water (35 c.c.) and the mixture refluxed till a clear solution was obtained. After heating for 15 mts. more, the mixture was cooled in an ice bath and the separated hydrochloride filtered off. It crystallised from dilute acetone in fine needles, not melting below 280°. The free base obtained from this crystallised from ethanol in rectangular prisms, m.p. 177–78° (Found: N, 15·47. $C_{15}H_{12}N_2Cl$ requires N, 15·58%).

4-(p-*Acetaminoanilino*)-6-*chloroquinaldine*.—This was prepared as described above by refluxing for 4 hrs., 4:6-dichloroquinaldine (1·5 g.) and *p*-aminoacetanilide (1·06 g.) in ethanol (25 c.c.). The crude condensation

product (2·37 g.), on crystallisation from ethanol separated in microscopic needles, m.p. 290–92° (Found: N, 12·85. $C_{18}H_{16}ON_3Cl$ requires N, 12·90%).

4-(p-*Aminoanilino*)-6-*chloroquinaldine*.—This was prepared by the hydrolysis of the foregoing acetamino compound. The free base crystallised from alcohol in prisms, m.p. 180–81° (Found: N, 14·36. $C_{16}H_{14}N_3Cl$ requires N, 14·81%).

4-(p-*Aminoanilino*)-6-*methoxyquinaldine*.—This was prepared as described above by condensing 4-chloro-6-methoxyquinaldine with *p*-acetaminoaniline and hydrolysing the resultant acetamino compound, m.p. 236–8°, with hydrochloric acid. The free base on crystallisation from acetone had m.p. 210–1° (Found: N, 14·78. $C_{17}H_{17}ON_3$ requires N, 15·05%). Slater[1] records m.p. 215°.

4-(p-*Aminoanilino*)-8-*methoxyquinaldine*.—This was prepared as above described by condensing *p*-aminoacetanilide (3·3 g.) with 4-chloro-8-methoxyquinaldine (4·5 g.) and hydrolysing the resultant acetamino compound (m.p. 243–4°, first melting at 170°) with hydrochloric acid. The free base crystallised from alcohol in prisms, m.p. 209–10° (Found: N, 14·91. $C_{17}H_{17}ON_3$ requires N, 15·05%).

2-(*p-Carboxyanilino*)-6-*methoxylepidine*.—An intimate mixture of 2-chloro-6-methoxylepidine (1 g.) and *p*-aminobenzoic acid (0·65 g.) was fused at 135° for 2·5 hrs. The cooled product was triturated with alcohol and filtered. The solid was purified by dissolving in sodium bicarbonate solution and precipitating from the clear filtrate with acetic acid. The compound obtained had m.p. 257–8° (Found: N, 8·88. $C_{18}H_{16}O_3N_2$ requires N, 9·09%).

2-(p-*Acetaminoanilino*)-6-*methoxylepidine*.—A mixture of 2-chloro-6-methoxylepidine (3 g.) and *p*-aminoacetanilide (2·1 g.) was maintained at 130° for 2·5 hrs. The reaction product on working up crystallised in prisms from alcohol, m.p. 215–7° (Found: N, 13·26. $C_{19}H_{19}O_2N_3$ requires N, 13·08%).

2-(p-*Aminoanilino*)-6-*methoxylepidine*.—This was obtained by hydrolysing the foregoing acetamino compound and basifying the hydrochloride (m.p. 280–2°) so obtained. The free base crystallised from acetone in prisms, m.p. 192–3° (Found: N, 15·04. $C_{17}H_{17}ON_3$ requires N, 15·05%).

4-(p-*Nitroanilino*)-7-*chloroquinoline*.—This was prepared by refluzing 4:7-dichloroquinoline (5 g.) and *p*-nitraniline (3·45 g.) in alcohol for 6 hours and working up the product. The product on crystallisation from chloroform separated in fine needles, m.p. 260–2° (Found: N, 13·90. $C_{15}H_{10}O_2N_3Cl$ requires N, 14·02%).

4-(p-*Aminoanilino*)-7-*chloroquinoline*.—The foregoing nitro compound (0·5 g.) was added gradually to a warm mixture of 10% acetic acid (50 c.c.) containing formic acid (0·5 c.c.) and iron powder (2 g.) and the mixture heated on the water-bath. On working up the mixture the amino compound, m.p. 176–7°, was obtained which showed no depression on admixture with the compound prepared by the other method described above.

4-(p-*Bromoanilino*)-7-*chloroquinoline*.—This was prepared by refluxing 4:7-dichloroquinoline (1 g.) and *p*-bromoaniline (1·2 g.) in alcohol and basifying the hydrochloride (m.p. above 290°) obtained. The base on crystallisation from acetone separated in fine white needles, m.p. 236° (Found: N, 8·29. $C_{15}H_{19}N_2BrCl$ requires N, 8·3%).

N^1-(p-*Acetaminophenyl*)-N^3-*isopropylthiourea*.—A mixture of isopropylisothiocyanate (3·6 g.), *p*-aminoacetanilide (5 g.) in alcohol (15 c.c.) was refluxed for 2 hrs. On working up the reaction mixture the thiourea was obtained crystallising from ethanol in prisms, m.p. 208–9° (Found: N, 16·89. $C_{12}H_{17}ON_3S$ requires N, 16·73%).

N^1-(p-*Aminophenyl*)-N^3-*isopropylthiourea* (*V*).—The foregoing acetyl derivative (12 g.) in 50% ethanol (200 c.c.) and con. hydrochloric acid (25 c.c.) was refluxed for about 30 mts., treated with charcoal and filtered. The filtrate was cooled and neutralised whereby the amino compound crystallised out. On recrystallisation from alcohol (yield, 6·7 g.), it had m.p. 145–7° (Found: N, 19·71. $C_{10}H_{15}N_3S$ requires N, 20·10%).

4-(p-N^1-*isopropylthiocarbamidophenyl*) *amino*-7-*chloroquinoline* (*IV*).—

(1) A mixture of 4:7-dichloroquinoline (3 g.), N^1-*p*-aminophenyl-N^3-isopropylthiourea (3·1 g.) and alcohol (50 c.c.) was refluxed on the steam-bath for 2 hours. When the reaction mixture was cooled, the hydrochloride of the condensation product separated in fine yellow plates. It was filtered, washed with cold water and dried (yield, 4·05 g., m.p. 226–9°). The hydrochloride, slightly soluble in acetone and alcohol and almost insoluble in most of the organic solvents was purified and crystallised from dilute alcohol, m.p. 233–5°. The free base obtained crystallised from dilute acetone and had m.p. 205–6° (dec.) (Found: N, 15·00. $C_{19}H_{19}N_4SCl$ requires N, 15·13%).

(2) A mixture of 4-(*p*-aminoanilino)-7-chloroquinoline (0·5 g.), isopropylisothiocyanate (0·2 g.) and alcohol (6 c.c.) was refluxed on the water-bath for 1 hr. The reaction mixture was cooled and further worked up as usual. The base obtained on crystallisation from alcohol had m.p. 158–65° but on crystallisation from dilute acetone had m.p. 205–7° (dec.) (Found:

N, 15·46. $C_{19}H_{19}N_4SCl$ requires N, 15·14%) and showed no depression on admixture with the sample prepared by method (1) described above.

When the above compound was treated with yellow oxide of mercury in alcoholic ammonia, desulphurisation took place even in cold but the compound isolated, m.p. 149–51° (Found: N, 12·28, 12·34; Cl, 19·5%; m. wt. 164; S absent) was not the desired guanidino compound which requires ($C_{19}H_{20}N_5Cl$) N, 19·80%. This compound showed depression in m.p. on admixture with 4-amino-7-chloroquinoline.

4-(p-N³-isopropylguanidino)-phenylamino-7-chloroquinoline.—A mixture of N^1-*p*-aminophenyl-N^3-isopropylthiourea (2 g.) was suspended in alcoholic ammonia (35 c.c. of 8%) and mercuric oxide (4 g.). The mixture began to turn dark rapidly and was allowed to stand overnight and filtered next day. The dark filtrate was treated with charcoal, and the guanidino compound obtained as such was treated with 4:7-dichloroquinoline (1·25 g.). The mixture was refluxed for 6 hours, and the solution concentrated to a small volume and treated with water whereby an oily product was obtained which did not readily crystallise. It was then converted into the picrate and the picrate crystallised from alcohol; m.p. 236–7° (Found: N, 18·6. $C_{19}H_{20}N_5Cl$, $C_6H_3O_7N_3$ requires N, 19·2%).

4:7-Dichloroquinoline did not condense with isopropylguanidine sulphate or with *m*-tolylguanidine sulphate.

4-(p-Guanidinophenyl)amino-7-chloroquinoline.—A mixture of 4:7-dichloroquinoline (3 g.), *p*-aminophenylguanidine sulphate (3 g. prepared by the action of S-methylthiourea sulphate on *p*-phenylene diamine) and alcohol (100 c.c.) was refluxed on the water-bath for 6 hrs. The reaction mixture was cooled, the crystalline solid that separated was filtered, washed with a little hot water and dried (yield, 2·45 g.). The free base liberated by the action of dilute sodium hydroxide solution (ammonia did not liberate the base) was crystallised from ethanol, m.p. 181–2° (Found: N, 21·43. $C_{16}H_{14}N_5Cl$ requires N, 22·47%). The hydrochloride on crystallisation from hot dilute alcohol separated in flakes, m.p. 220° (Found: N, 17·2; Cl, 25·68. $C_{16}H_{14}N_5Cl$, 2 HCl requires N, 18·2; Cl, 27·7%; $C_{16}H_{14}N_5Cl$, 2 HCl, H_2O requires N, 17·39; Cl, 26·89%).

Summary

Attempts made to evolve a general method for the synthesis of 4-(guanidylphenylamino) quinoline derivatives of formula (II) are described. By reacting 4-chloro-6-methoxyquinaldine, 4-chloro-8-methoxyquinaldine, 4:6-dichloroquinaldine and 4:7-dichloroquinoline individually with *p*-acet-

phenylediamine were obtained respectively 4-(*p*-acetaminoanilino)-6-methoxyquinaldine, 4-(*p*-acetaminoanilino)-8-methoxyquinaldine, 4-(acetaminoanilino)-6-chloroquinaldine and 4-(*p*-acetaminoanilino)-7-chloroquinoline. On hydrolysis, these furnished the corresponding amino derivatives. *p*-Nitraniline condensed with 4:7-dichloroquinoline to furnish 4-(*p*-nitroanilino)-7-chloroquinoline which on reduction with iron and acetic acid yielded the corresponding amino compound identical with that reported above. *p*-Bromoaniline also easily condensed with 4:7-dichloroquinoline. In contrast to the reactivity of the 4-chloroquinolines, the 2-chloro analogues were very sluggish and condensed with aromatic amines only under drastic conditions.

The reaction of 4-(*p*-aminoanilino)-7-chloroquinoline with isopropylisothiocyanate as well as the condensation of 4:7-dichloroquinoline with *p*-aminophenylisopropylthiourea (V) furnished the thiourea derivative (IV) which on desulphurisation with mercuric oxide in alcoholic ammonia did not furnish the corresponding guanidine compound. This was obtained however by the action of N^1-isopropyl-N^3-*p*-aminophenylguanidine on 4:7-dichloroquinoline. The latter also reacted with *p*-aminophenylguanidine to furnish the corresponding guanidine of formula (II). This method appears to be of general applicability for the preparation of quinilinoaminophenylguanidine derivatives of formula (II).

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